OPTIMISATION OF ALKALI-FUSION PROCESS FOR ZIRCON SANDS:

A KINETIC STUDY OF THE PROCESS

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ABSTRACT

Zirconium chemicals are attracting increasing interest owing to the growing number of applications for speciality chemicals and the low toxicity of zirconium chemicals. Currently, the main source of zirconium chemicals is zircon. Zircon beneficiation is complex due to its high thermal and chemical stability. Zircon also contains radioactive impurities caged in its structure. In classic methods, these impurities are removed by means of various precipitation processes, which are reportedly both time-consuming and inefficient. The De Wet process represents an improved zirconium chemicals recovery process that starts from zircon. In this approach, the radioactivity is effectively and efficiently leached from a solid phase.

The present study was, however, concerned primarily with the optimisation of the alkali fusion step in the De Wet process of zirconia and zirconium chemicals recovery. For this purpose, fusions were conducted using varying fusion temperatures, reaction times and reagent ratios. Fusion times were varied from 1 to 336 hours at temperatures from 600 to 850 °C. Stoichiometric ratios ranging from 1 to 6 mols of sodium hydroxide per mol of zircon were investigated.

The 336-hour fusions were used to identify the equilibrium phases that form at each temperature. Below 650 °C, only sodium zirconate (Na_2ZrO_3) is observed in the reaction mixture. Above 700 °C, sodium zirconium silicate (Na_2ZrSiO_5) is also present in the product spectrum. The relative abundance of these two zirconium chemicals is dependent on the stoichiometry. Below 2 mols of sodium hydroxide, sodium zirconium silicate is virtually the sole phase that forms. Above this level, the sodium zirconate content increases with the amount of sodium hydroxide per mol of zircon. At 6 mol of sodium hydroxide, it is the only zirconium-containing phase observed.

Both equilibrium compounds can be used to recover zirconia. Sodium zirconate requires more base for its formation, but hydrolyses efficiently in water to hydrous zirconia. This allows the recovery of the alkali reagent as a saleable product stream. The formation of sodium zirconium silicate consumes only half the amount of base required for sodium zirconate. However, it is insoluble in water and hydrolyses only in acid media. Thus its presence in the fusion product leads to reduced alkali recovery, increased acid reagent consumption and higher volumes of salt waste.

From a practical point of view, short fusion times are preferred and are also more cost-effective. The zirconia yield showed a temporal maximum at 2-hour fusions. With this fusion time, optimum recovery of zirconia, as well as salt waste minimisation, was achieved by fusing at 850 °C in a 2:1 reagent mol ratio mix.

Impure zirconia can also be obtained directly by calcining the solid residue that remains after the following sequence of steps: fusion, water leach, dilute acid hydrolysis and, finally, water wash. A product containing 79% zirconia was obtained in this way after fusing for 8 hours at 850 °C with a 4:1 mol ratio.

OPSOMMING

Sirkoniumchemikalië lok toenemende belangstelling as gevolg van nuwe toepassings in spesialiteitschemikalieë en die lae giftigheid van sulke verbindings. Die hoofbron vir sirkoniumchemikalië is tans sirkoon. Die hoë termiese en chemiese stabiliteit van sirkoon bemoeilik egter chemiese opgradering. Sirkoon bevat ook radioaktiewe onsuiwerhede in sy struktuur. In die klassieke herwinningsmetodes word hierdie onsuiwerhede verwyder deur middel van duur en tydrowende presipitasieprosesse. Die De Wet proses behels 'n verbetering op die bestaande sirkoonherwinningsprosesse. In hierdie proses word die radio-aktiwiteit effektief en kostedoeltreffend vanuit 'n vastestoffase uitgeloog.

Hierdie studie was egter hoofsaaklik gemoeid met die optimisasie van die alkali-smeltingsstap in die De Wet proses vir die herwinning van sirkoniumchemikalieë. Vir hierdie doel is alkalifusie by verskillende temperature, reaksietye en reagensverhoudinge uitgevoer. Fusietye is gevariëer van 1 tot 336 ure by temperature van 600 tot 850 °C. Stoïgiometriese verhoudings vanaf 1 to 6 mol natriumhidroksied per mol sirkoon is ondersoek.

Die 336-uur smeltings is gebruik om die ewewigsreaksieprodukte by verskillende temperature te identifiseer. Daar is gevind dat onderkant 650 °C natriumsirkonaat (Na_2ZrO_3) as die enigste sirkoniumproduk in the reaksiemengsel vorm. Bokant 700 °C vorm natriumsirkoniumsilikaat (Na_2ZrSiO_5) as tweede produk. Die relatiewe verhouding van hierdie twee produkte in die hoë-temperatuursmeltsel is afhanklik van reagensstoïgiometrie. Wanneer dit onder 2 mol natriumhidroksied per mol sirkoon is, vorm slegs natriumsirkoniumsilikaat. Bokant hierdie vlak vorm daar wel ook natriumsirkonaat. Met 6 mol natriumhidroksied per mol sirkoon, is laasgenoemde die enigste sirkoniumbevattende produk wat vorm.

Beide reaksieprodukte is geskik vir die herwinning van sirkoniumchemikalieë vanaf sirkoonsand. Natriumsirkonaat benodig 'n groter hoeveelheid van die reagens maar dit hidroliseer geredelik in water om 'n neerslag van sirkoniumhidroksied te vorm. Dit vergemaklik die herwinning van die alkalië in die vorm van 'n verkoopbare natriumsilikaatproduk. Die vorming van natriumsirkoniumsilikaat verg minder natriumhidroksied. Die produk is egter nie oplosbaar in water nie en sure word benodig om dit te hidroliseer en die sirkonia vry te stel. Dus sal die teenwoordigheid daarvan in die

reaksieproduk lei tot verminderde alkaliherwinning, groter verbruik van suur veroorsaak en ook lei to hoër volumes van die soutafvalstroom.

In die praktyk word kort fusietye verkies wat ook kostebesparing teweeg bring. Die sirkoniaherwinning wys ‘n tydelike maksimum by die 2-uur punt. By hierdie fusietyd gee ‘n reaksietemperatuur van 850 °C en ‘n 2:1 reagensmolverhouding optimale herwinning van sirkonia en minimale soutvorming.

Onsuiwer sirkonia kan ook direk vanaf die fusieproses verkry word deur kalsinering van die vastestofresidu na die volgende prosesstappe: waterloging, suurhidrolise en waterwas. ‘n Produk wat 79% sirkonia bevat is verkry na fusie vir 8 uur by 850 °C en ‘n 4:1 stoïgiometriese molverhouding.

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1. INTRODUCTION

Zirconium and its compounds have in recent years received increasing attention, due to new fields of application. Zirconium chemicals are used in, amongst others, refractories, foundry moulds, glaze opacifiers, the glass industry, abrasives, ceramics and ceramic colours, piezoelectrics, capacitors, pyroelectrics, solid electrolytes, the oil industry, wool flame-proofing and water-proofing, photography, the textile industry, medicine and cosmetics [1-8]. Zirconium's silicate salt is used for the immobilisation of wastes with actinides [8-10]. Most of these applications are related to zirconia, the oxide of zirconium IV.

Historically, zirconium did not receive much attention because it had few industrial applications in early times. Zircon[1], the main source of zirconium, was first known in zirconium compounds, as *hyacinth, jargon, jacinth, ligure, diamante brut or clarus hyalinus* in the Middle Ages [2, 3, 7, 11, 12]. The mineral is also mentioned in biblical writings. In addition, it was believed to be an imperfect diamond, called a *Matara Diamond* [1]. It was Werner who gave it the name zircon [7, 11].

In 1789, Klaproth fused zircon with sodium hydroxide and extracted the product with hydrochloric acid. In the solution, he found an element that exhibited novel behaviour [2, 12]. Berzelius was the first to extract zirconium, in 1824 [2, 12]. Lely and Hamburger prepared the first relatively pure zirconium, in 1904 [12]. Really pure zirconium was prepared only in 1925, by Van Arkel-De Boer using the iodide method [13].

Naturally occurring zirconium compounds contain small amounts of hafnium, about 2%. Their complete separation is very difficult due to their essentially identical atomic and ionic radii. This leads, essentially, to their having identical chemical properties [14]. There are only a few ores rich in hafnium, namely alvite, with 13.6%, and thortveitite, with 2.7% [13]. Ores with a zirconium content of more than 95% have been found associated with tantalum ore in Mozambique [12]. Ryshkewitch and Riecherson [5] reported ores with concentration runs of HfO_2 up to 22%. In most applications, zirconium chemicals can be used with their hafnium impurities. Ores with high levels of hafnium also have high levels of radioactive impurities [12]. The need to produce pure zirconium, for atomic application, and pure hafnium was the

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[1] Mineral in which the major component is $ZrSiO_4$.

motivation for developing the extraction technology and this made possible the production of several zirconium chemicals [2, 12], of which zircon and zirconia were the first to find application [2].

1.1 Aim of the Study

There is an increasing demand for zirconium chemicals. Inexpensive methods for the recovery of zirconium and zirconium chemicals from the most abundant and cheapest source, zircon, need to be found and optimised.

Zircon is widely found all over the world in beach sands, which are constantly being formed. Beach sand is undoubtedly the most abundant and inexpensive raw material for zirconium and zirconium chemicals [2, 3, 12]. The major problem with zircon is its high chemical stability and the high level of impurities encaged in the structure. The chief impurities are iron, aluminium, silicon, nickel and titanium, apart from radioactive impurities such as uranium and thorium [2, 3, 5, 13, 15, 16].

The extreme chemical and thermal stability of zircon can be explained by the high coordination of bisdisphenoid ZrO_8 in a tetragonal structure with SiO_4 tetrahedra [10, 17]. Zircon therefore requires aggressive reaction conditions for decomposition [2, 6, 12]. Decomposition of zircon with alkali at high reaction temperatures is a well-known procedure [2, 6, 12, 15]. De Wet and his team have developed a novel process of recovering zirconia from zircon sands using this reaction. Compared with conventional processes, the De Wet process has the following advantages [3, 16]:

- Fewer process steps are needed to manufacture acid zirconium sulphate tetrahydrate (AZST)
- A comparatively low-cost pigment-suitable zirconia with reduced radioactivity content can be made.
- The alkali reactant can be recovered in the form of a saleable, radioactivity-free, sodium silicate product stream.
- Sulphuric acid is used in economical quantities in the manufacture of AZST; the overall process requires less than 5% stoichiometric excess of sulphuric acid.

- The radioactivity is leached out of a solid phase instead of using precipitation steps that require chemical additions and generate much waste.
- There are fewer effluent streams and less waste to discard.

In this study, a kinetic analysis was undertaken with the aim of optimising the recovery of zirconia during the alkali fusion step of the De Wet process, bearing in mind that zirconia can be utilised as a starter material for the production of other zirconia chemicals and that it is also the most important zirconium chemical.

The optimisation included determining the optimum fusion temperature, i.e. the temperature at which the conversion can be considered as maximum for the process, taking into consideration time and production costs. Secondly, the appropriate mol ratio for optimum conversion was sought. A constant guideline for this study was that an industrial process must be effective in terms of both time and costs.

1.2 Methodology

The research was undertaken at the Institute of Applied Materials, University of Pretoria, with financial support from the THRIP programme of the Department of Trade and Industry and the National Research Foundation (NRF) of South Africa, as well as from Kumba and Xyris Technology CC.

The main objective of the study was to optimise the alkali fusion step in the De Wet process. For that purpose, the research was divided into three different steps as follows:

- **Literature review**. Using existing facilities, conventional methods of recovering zirconia from zircon sands were reviewed. The aim here was to acquire knowledge of this specific problem, and how the research results could be applied to solving this problem.
- **Experimental step**. This consisted of practical laboratory work to obtain results.
- **Evaluation of the results**. The results obtained were assessed in relation to whether the research objectives had been achieved.

2. PROPERTIES OF ZIRCONIUM

2.1 Physical Properties

Zirconium is the 40th element in the periodic table. It belongs to the titanium subgroup, subgroup IVB, in which hafnium is also placed. Zirconium occurs naturally in the form of five isotopes with mass numbers of 90, 91, 92, 94 and 96 and corresponding natural abundances of 51.46%, 11.23%, 17.11%, 17.40 and 2.80% respectively [13]. A further 26 zirconium radioisotopes occur in the degradation series of other elements [7]. The name zirconium comes from the Persian word *zargun*, which means gold-like metal [7, 18].

Table 2.1: Physical properties of zirconium [12, 14]

Relative atomic mass		91.224
Atomic radius		15.90 nm (in metal lattice)
Ionic radius (Zr^{4+})		7.5 nm
Electronegativity		1.22
Standard potential M/MO_2		1.53 V
Melting point		1 852 ± 2 °C
Boiling point		3850 °C
Density	α -phase	6.50 g/cm^3
	β-phase	6.05 g/cm^3
Specific heat at 25 °C		0.285 $Jg^{-1}kg^{-1}$
Thermal conductivity at 25 °C		21.1 $Wm^{-1}K^{-1}$
Thermal expansion at 25 °C (α)		5.89×10^{-6} K^{-1}
Ionisation potential	1st	674.1 kJ mol^{-1}
	2nd	1 268 kJ mol^{-1}
	3rd	2 217 kJ mol^{-1}
	4th	3 313 kJ mol^{-1}
Effective cross-section for thermal neutrons		$1.9\times10^{-29}m^2$ (0.19 barns)
Thermal conductivity at 25 °C		21.1 $Wm^{-1}K^{-1}$
at 100 °C		20.4 $Wm^{-1}K^{-1}$
at 300 °C		18.7 $Wm^{-1}K^{-1}$

Zirconium is a lustrous metal, hard and ductile, with the appearance of stainless steel, in the form of either platelets or flakes. In powder form, the colour is bluish-black. Pure zirconium shows three solid phases. The ω-Zr phase is stable below 200 K, 1 atm and up to 200 K at 6 GPa. The α-Zr phase is stable between 200 K and 1 125 K. The β-phase is stable from 1 125

K up to the melting point [12, 14]. Some important physical properties of zirconium are summarised in Table 2.1.

Zirconium is an elastic metal, like other metals with lower melting points. Its strength diminishes with increasing temperature. The presence of contaminants and a crystalline texture influences its properties. Small amounts of contaminants can drastically reduce its corrosion resistance [12, 13].

2.2 Chemical Properties

Zirconium is able to form compounds with 1, 2, 3 or 4 valences. Oxidation states lower than 4 are difficult to find. Zirconium compounds commonly exhibit coordination numbers of 4, 6, 7 and 8, with tetrahedral, octahedral, pentagonal bipyramidal and dodecahedral forms respectively. Crystalline structures, featuring coordination numbers equal to 7 or 8, with capped trigonal prismatic and square antiprismatic forms respectively, are also known [14, 15, 18].

Considering that in stereochemistry zirconium ions are found to be highly charged, spherical and very large, with no partially filled shells, it is understandable that compounds of zirconium (IV) have high coordination numbers (6, 7 and 8) and a great variety of coordination polyhedra [2, 14]. A further consequence of the high charge-to-radius is that the aqueous solution chemistry is dominated by hydrolysis and the presence of polymeric species. These species are sensitive to their environment and their equilibrium is established slowly, making study results difficult to obtain. The practical effect of this is that it is difficult to control the production of zirconium chemicals with consistent properties [2].

Zirconium forms one stable oxide, with an oxidation number equal to 4 (ZrO_2). Oxygen dissolved in the zirconium metal lattice makes it possible to discover some low oxides, such as $ZrO_{0.3}$. Zirconium monoxide has been detected in some stars by mass spectrographic measurements and it can also be found evaporated on the surface of tungsten filaments [5, 12, 13, 15]. Other oxygen pseudo-compounds can be observed when oxygen is added in the form of alpha zirconium. Those pseudo-compounds represent oxygen dissolution in the zirconium lattice [15]. New research results have indicated that zirconium monoxide is produced by the reduction of zirconium dioxide with magnesium; indeed some studies refer to it as the major phase produced [19]. However, electrochemical studies have questioned the existence of this species, suggesting that zirconium monoxide may be a mixture of zirconium and zirconium dioxide [20].

When a hydroxide solution is added to a solution of zirconium (IV), a white gelatinous precipitate is generated, $ZrO_2.nH_2O$. The water content is variable. The existence of true hydroxides is disputed [14]. Nevertheless, hydrous zirconium dioxide has been accepted as equivalent to zirconium hydroxide. Huang *et al.* [21] have established the differences between hydrous zirconium dioxide and hydrated zirconium hydroxide, $Zr(OH)_4.nH_2O$, on the assumption that zirconium hydroxide does exist. Baddeleyite, zirconia in monoclinic (form, has a structure in which the metal atom exhibits a coordination number equal to 7 [14].

Chemically, zirconium is highly reactive – in air or in aqueous media, it promptly develops an oxide film, which makes it stable with regard to corrosion. The stability can, however, be drastically reduced by fluoride ions, even in trace amounts [12].

Zirconium is stable in both acid and caustic media. At high temperatures it is attacked slowly by aqua regia, phosphoric acid, hydrofluoric acid and sulphuric acid. At high concentrations in acidic media, zirconium may be attacked rapidly. It is also attacked by molten sodium bisulphate, sodium carbonate and sodium peroxide. The formation of a black film protects it against molten sodium hydroxide. Zirconium is totally resistant to corrosion by organic acids [13].

Compounds in which zirconium forms an oxy-anion are called zirconates. These compounds can be obtained by combining oxides, hydroxides and nitrates of other metals with similar zirconium compounds and firing the mixtures at 1 000 to 2 500 °C. The salts are, in fact, mixtures of metal oxides. Discrete zirconate ions are not known [14].

With zirconium, the other elements of the oxygen group form compounds similar to zirconia, ZrY_2, where Y can be sulphur, selenium or tellurium. Those compounds are semiconductors [14].

Zirconium metal reacts with CO_2, CO, SO_2, steam, nitrogen and nitrogen oxides more slowly than with air. At higher temperatures, zirconium reacts with hydrogen, oxygen, nitrogen and halogens. The reaction with hydrogen is reversible. When finely divided, it is pyrophoric. Zirconium powder reacts with many other elements, such as hydrogen, boron, carbon, nitrogen and the halogens. The ignition temperature for the process is above 200 °C. The reaction of platinum and zirconium powder is violent [12, 13, 15].

Zirconium forms alloys with various metals. It can also be added in small amounts to other metals to enhance their properties [12, 13].

In aqueous media, zirconium ions tend strongly to hydrolyse. This is attributed to the high charge of the ions. Free ions exist at very low concentrations ($\approx 10^{-4}$ M) and high acidity (1-2 M of $[H^+]$) [14]. The stability of zirconium in the electrochemical series lies below that of water, suggesting that zirconium will decompose in water through the evolution of hydrogen, dissolving as zirconic ions (Zr^{4+}) and zirconyl ions (ZrO^{2+}) in very acid solutions, and as zirconate ions ($HZrO_3^-$) in very alkaline solutions. In moderately acid, neutral and moderately alkaline solutions, the metal will be covered with a thin film of oxide [20].

Because of the low value of the reduction potential of zirconic, zirconyl and zirconate ions with respect to metallic zirconium, the electrolytic separation of zirconium from aqueous solutions is not practicable. Molten salts (potassium zirconifluoride or a mixture of zirconium and sodium chlorides) can be electrolysed to give an impure powdery metal. Zirconium can be displaced by zinc in solutions of anhydrous zirconium sulphate in methyl alcohol [20].

Zirconium forms basic salts with sulphates and chromates. These salts contain infinite chains of composition $[M(\mu\text{-}OH)_2]_n^{2n+}$. The coordination number of the metal in those complexes rises to 7 and 8 [14].

Zirconium can exhibit other oxidation states, but no free ions are known to exist in those states. For oxidation state III, trihalides are known, namely $ZrCl_3$, $ZrBr_3$ and ZrI_3. There are several methods of synthesis. One of them involves the reduction of ZrX_4 in molten AlX_3, with aluminium or zirconium. Zirconium halides are reduced faster than hafnium halides. This process can therefore be used to separate zirconium from hafnium contaminants. [14].

Lower oxidation states than III do exist. Compounds such as ZrCl and ZrBr are obtained by reaction of ZrX_4 with zirconium metal at 800 to 850 °C. These compounds have high thermal stability, with a melting point above 1 100 °C. They have a metallic character and cleave like graphite. Both compounds may incorporate oxygen or hydrogen [14]. Halides of zirconium (II) and zirconium monoxide are also known [14]. Halides can be made through the reduction of ZrX_4 (where X can be chlorine, bromine or iodine) with zirconium metal in sealed tantalum containers [14].

2.3 Toxicity of Zirconium

Zirconium seems to be non-toxic as an element and in its compound forms. Physiologically, the pH of zirconium is associated with biological activity, but it is inert in human tissue. For this reason, some of its compounds have been used in the cosmetics industry. Zirconium applied in antiperspirants has been found to be a probable cause of skin and lung granulomas [12].

Strongly acidic compounds of zirconium, such as zirconium tetrabromide, tetrachloride, tetrafluoride, tetraiodide, tetranitrate and sulphate, are strongly corrosive to the eyes, lungs, skin, mouth, oesophagus and stomach. That is due to the compound's acidic nature, which can lead to hydrolysis in contact with animal and plant tissue [12].

The oral toxicity is very low, the maximum for pulmonary exposure being at a level of 5 mg of zirconium per m^3 [15].

Although metallic zirconium is non-toxic, finely divided zirconium metal (powder, dust, chips, foil, sponge) must be handled with care because it is easily ignitable in air. Workers dealing with zirconium chips or other forms of finely divided zirconium should wear heat-reflectant clothing [12].

A zirconium fire can only be extinguished by disrupting the oxygen supply. Other oxidants, such as water, carbon dioxide, carbon tetrachloride, iron oxide and limestone, must be removed to control a zirconium fire. Small fires can be smothered by dousing with dry silica sand or dry table salt, or by using argon or helium if the zirconium is in a closed container. Large-scale fires are allowed to burn out, while protecting the surroundings from ignition. The use of water is strictly prohibited in zirconium fires [12].

Finely divided zirconium metal is classified as a flammable solid and specific regulations are prescribed for its transportation [15].

Solutions that corrode zirconium metal react violently or explosively with finely divided zirconium [12]. In terms of sensitivity, zirconium is an eye irritant [7].

2.4 Industrial Importance of Zirconium Chemicals

2.4.1 Zirconium basic sulphate

This is a key product in the production of pure zirconium chemicals because it is possible to control the form in which it is precipitated. It can be obtained by reducing the acidity of zirconium sulphate solution. The basis of the formation of zirconium basic sulphate is related to the fact that the dissolution of zirconium sulphate sheets occurs by breaking the bonds between sulphate groups and zirconium atoms, via replacement of the sulphate groups with hydroxy groups as ligands. The structure is composed of single strands of $[Zr(OH)_2]_n^{2n+}$, joined by bridging sulphates [2, 16].

In this compound, zirconium atoms predominantly have a coordination number of 8. The most common zirconium basic sulphate is $Zr_5O_7(SO_4)_3.nH_2O$. Other basic sulphates have been formulated in the literature. The dodecahedral structure consists of layers of ZrO_8 bridged by sulphate ions. Another zirconium basic sulphate, $Zr(OH)_2SO_4$, has a square antiprism and is composed of infinite zigzag chains of $[Zr(OH)_2]$ [12, 13].

Sulphate ions have a strong affinity for zirconium and therefore other sulphate salts of zirconium are known, as well as various anionic sulphato-complexes in solutions. These salts are referred to as normal salts to distinguish them from the basic and acid salts. The key to this definition lies in the SO_4/Zr ratio. If this ratio is equal to 2, the salt is defined as neutral or normal, although these salts exhibit a strongly acidic behaviour. If the ratio is less than 2, then the salt is referred to as basic (in contrast to acid); these salts are also called anionic salts [12, 13, 16, 22].

Zirconium orthosulphate solutions are highly acidic. They can be made from zirconium basic sulphate or carbonate, or by the direct dissolution of baddeleyite in sulphuric acid. The salt crystallises directly from the solution in the form of a tetrahydrate, $Zr(SO_4)_2.4H_2O$. By heating it at 100 °C, the tetrahydrate can be converted to a monohydrate and from a monohydrate it becomes anhydrous at 380 °C [2, 12, 13, 22]. Higher hydrates are also known [13].

Zirconium basic sulphate is used in the production of zirconium basic carbonate and zirconium hydroxide, and therefore to produce zirconia via zirconium hydroxide. It is also used to produce the so-called zirconium soaps, which are paint driers. Fresh zirconium sulphate solutions are preferred for use in leather tanning over chromium solutions. Mixtures of sulphate solutions of chromium, zirconium and aluminium have been proposed. Zirconium sulphate is used in photography, as a pigment coating and in the treatment of wool-fabric to confer flame resistance. Zirconium sulphate is also used in the catalysis of many reactions related to hydrocarbon processing in oil refineries, where it is referred to as a most active catalyst [2, 12, 15, 16, 23].

2.4.2 Zirconium carbonate

From the theoretical point of view, there are two kinds of carbonate salts of zirconium: the normal and the basic salts. In practice, only basic salts are known [13]. Nominally, basic zirconium carbonate is $2ZrO_2.CO_2.xH_2O$. The ratio of ZrO_2 to CO_2 may range from 4:1 to 1:1 [15].

It is produced in a two-step process. First, zirconium sulphate is produced from an oxychloride salt solution. The carbonate is formed through an exchange reaction between the water slurry of zirconium basic sulphate and sodium carbonate or ammonium carbonate at 80 °C, under controlled pH conditions [15, 16].

Freshly produced zirconium hydroxide dispersed in water can easily absorb carbon dioxide to form zirconium basic carbonate. Once washed free of other anions, it can be dissolved in organic acids such as acetic to form the corresponding oxysalts [15].

Ammonium zirconium carbonate enhances the fungicidal action of copper salts on cotton cloth, and zirconium acetate has been used as an algaecide. Both zirconium carbonate and zirconium oxyacetate have been used in the waterproofing of fabrics. Zirconium carbonate is also used in floor polishes [15].

2.4.3 Zirconium chlorides

Zirconium oxide dichloride, $ZrOCl_2.8H_2O$, commonly called zirconium oxychloride, is really a hydroxyl chloride, $[Zr_4(OH)_8.16H_2O]Cl_8.12H_2O$. It is commercially produced by the caustic fusion of zircon. The cake is then washed with water. Sodium zirconate hydrolyses to hydrous zirconia, which is reacted with hot hydrochloric acid. Zirconium oxychloride is recovered by crystallisation. Zirconium oxychloride can also be produced by the dissolution of zirconium tetrachloride in water, or by reacting zirconium carbonate with hydrochloric acid [2, 12, 15, 16, 24].

Zirconium oxychloride is an important basic material in the production of other zirconium chemicals. The salt cannot be dried to the anhydrous form; it decomposes to hydrogen chloride and zirconium oxide. Anhydrous zirconium oxychloride is produced by reaction of dichlorine oxide (phosgene) with a zirconium tetrachloride suspension in carbon tetrachloride. The reaction starts at –30 °C. The compound is solid and extremely hygroscopic; it decomposes to zirconia and zirconium tetrachloride at 250 °C [15].

Zirconium tetrachloride is produced by zirconia carbochlorination, or by reacting zirconium metal with chlorine, hydrogen chloride or phosgene. Chlorinated hydrocarbons, particularly carbon tetrachloride, chloroform or hexachloroethane, can be used as chlorinating agents on a laboratory scale. Zirconium tetrachloride is also formed by reacting ferrozirconium or silicozirconium with iron (II) chloride at elevated temperatures [12, 15].

Zirconium tetrachloride reacts rapidly with water, vapour or liquid to exchange two chlorines for oxygen. In powder form, it reacts in water to form zirconium hydroxychloride and free hydrochloric acid [12, 15].

Zirconium tetrachloride is used to produce zirconium organometallic compounds, e.g. reacted with alcohols to form alkoxides, to form zirconium nitride coatings, and electrochemically transformed into zirconia at high temperatures in fuel cells [2, 12].

Zirconium hydroxychloride and oxychloride are used in the oil industry to stabilise the oil viscosity, and as a clay stabiliser, in wool flameproofing, and in antiperspirants [2].

2.4.4 Zirconium fluorides

Mixing hydrogen fluoride and zirconium tetrachloride at 350 °C produces anhydrous zirconium tetrafluoride, ZrF_4. The zirconium produced in this way has high purity. Hydrofluorination of zirconia at 25 °C, followed by a purifying sublimation in hydrogen fluoride at 825 °C, is another method of processing zirconium tetrafluoride. Direct fluorination of the metal is not indicated due to the low volatility of zirconium tetrafluoride, which coats the surface of the metal. The reaction has to be done at 800 °C to avoid coating the surface [12, 15].

Anhydrous zirconium tetrafluoride with very high purity is a major constituent of some fluoride glasses. These glasses have been specially developed because of their transparency in the near-UV (ultraviolet) to mid-IR (infrared), 0.3-6 µm range. The glasses are held to be better than those of quartz optical fibre. Potassium hexafluorozirconate is used to introduce zirconium into molten aluminium and magnesium as a grain refiner. It is also used in wool flameproofing and in metal conversion coatings [2, 12, 15].

2.4.5 Zirconium phosphates

All phosphates of the titanium group precipitate in strongly acidic solutions. This is important in the analytical separation of zirconium from other elements and in preparing zirconium phosphate. The salt precipitates in gelatinous amorphous form, with variable composition. If the precipitate is refluxed in strong phosphoric acid, a crystalline and stoichiometrically constant compound, $Zr(HPO_4)_2.H_2O$, is obtained. Zirconium bis (monohydrogen phosphate) can also be obtained by gradual precipitation of the phosphate from heated zirconium fluoride solution [13, 15]. Zirconium phosphate hydrolyses in strong basic media to give hydrous zirconia [15].

Zirconium phosphate absorbs caesium and other radioactive-decay products. For this reason, it has been proposed for use as part of permanent disposal systems for nuclear fuel waste processing. Sodium hydrogen zirconium phosphate is used in portable kidney dialysis systems to regenerate and recirculate the dialysate solution. The solution picks up urea during the dialysis. Urea reacts with urease to form ammonia, which is absorbed by sodium hydrogen zirconium phosphate [2, 13, 15]. Zirconium phosphate can act as an intercalation compound because of its structure and bonding between the layers [12].

2.4.6 Zirconium hydride

Zirconium hydride, ZrH_2, is prepared by the reversible absorption of hydrogen on a heated zirconium surface (sponge or ingots). The metal is heated above 600 °C in an inert atmosphere or a vacuum to remove the surface oxide film [12].

Zirconia can also be reduced by calcium hydride to form zirconium hydride. This method produces a fine powder (2 - 5 μm) for use in pyrotechnics, such as fuses or fireworks [12].

Zirconium hydride is not a true compound with a fixed stoichiometry, but a series of crystalline phases in which zirconium metal transforms with changing hydrogen concentration and temperature. Most commercial zirconium hydride powder contains 60 - 64% and more of hydrogen [12, 15].

Zirconium hydride has been used in the nuclear industry as a moderator for thermal neutrons in compact, high-temperature reactors. It is also of interest for hydrogen storage and nickel-based hydrogen battery applications [12].

2.4.7 Zirconium nitrides

Zirconium nitride, ZrN, is a gold-coloured, hard, brittle metallic nitride. It is thermally and chemically stable, and has low resistivity. It is an interstitial compound with a NaCl-type cubic structure [12, 15].

Zirconium nitride is prepared by heating zirconium loose sponge or zirconium hydride to 1 100 – 1 500 °C in a nitrogen or ammonia atmosphere. The reaction rate is limited by the slow rate of nitrogen diffusion into the nitride protective layer. Stoichiometric nitrogen amounts require time and high temperatures [12, 15].

Zirconium nitride has been used as a wear-resistant coating on steel drills and cemented-carbide tool bits, as a decorative coating, as a protective coating on steel vessels handling molten metal, and as a surface film on solar energy collectors [12]. In some of these applications, it is being replaced by its analogues titanium nitride, and hafnium nitride [15].

2.4.8 Zirconium carbide

Zirconium carbide, ZrC, is a hard dark-grey brittle solid. It is an interstitial carbide with carbon atoms occupying the octahedral interstices of the zirconium lattice. It is made by the carbothermic reduction of zirconia in an induction-heated vacuum or a hydrogen atmosphere furnace at 1 600 °C. The zirconium carbide produced in this way is porous and light. Milling it and refiring it above 2 200°C produces a dense powder. It can also be produced from zircon by reduction with coke in an electric arc furnace. Heating zirconium tetrachloride with methane in a hydrogen atmosphere at 1 200°C deposits zirconium carbide. Pure zirconium metal and fine graphite powder react exothermically to form zirconium carbide; the reaction needs to be initiated [12, 15].

Zirconium carbide is inert to various reagents. It is dissolved by hydrofluoric acid solutions that also contain nitrate or peroxide ions, and by hot sulphuric acid. It reacts with halogens above 250 °C to form zirconium tetrahalides. It oxidises to zirconium dioxide in air at above 700 °C. Zirconium carbide is an electrical conductor and does not hydrolyse in water. It melts at 3 420 °C [13, 15].

Because it is hard, with a high melting point, zirconium carbide has been under consideration as a constituent of uranium carbide fuelled reactors. It is also used in tool bits in thin film form [13, 15].

2.4.9 Zirconium borides

Three borides of zirconium are known from the zirconium-boron system, namely zirconium monoboride, ZrB, zirconium diboride, ZrB_2, and zirconium dodecaboride, ZrB_{12}. Zirconium diboride is the only one that is chemically and thermally stable. It is a grey refractory solid with a hexagonal crystal structure and melts at 3 245 °C. It is considered to have the best oxidation resistance of all refractory hard metals. Zirconium diboride also has excellent thermal shock resistance [12, 15].

Technical-grade zirconium diboride can be produced by reacting zircon, boron oxide and carbon in a submerged-electrode arc furnace. The pure compound is produced by co-reduction of zirconium tetrachloride and boron trichloride with hydrogen or aluminium in a chloride bath. Another process consists of a carbothermic reduction of zirconia and boron carbide. The use of boron oxide in this process is not appropriate because of its relatively high vapour pressure under working conditions (1 400 °C) [12, 15]. In the film form, it is produced by subliming zirconium tetrahydridoborate at 25 °C in a vacuum and passing the vapour over the substrate heated to 250 °C [12].

Zirconium tetrahydridoborate, $Zr(BH_4)_4$, is prepared by the reaction of zirconium tetrachloride with lithium tetrahydridoborate in diethyl ether, followed by double distillation at 20 °C. It has a tetrahedral structure, with three hydrogen atoms bridging the zirconium atom and each boron atom [12].

Zirconium tetrahydridoborate is one of the most volatile zirconium compounds: it melts at 29 °C and boils at 118 °C. Its vapour pressure at 25 °C is 2 kPa. It decomposes near 250 °C, forming zirconium boride and it ignites in contact with dry air [12].

Zirconium diboride is used as a diffusion barrier in semiconductors, as a container for molten metals, and as a burnable absorber in nuclear reactor cores. Zirconium tetrahydridoborate catalyses the polymerisation of unsaturated hydrocarbons, and reacts with aliphatic alcohols to form zirconium and boron alkoxides [12].

2.5 Analytical Aspects of Zirconium

Zirconium is qualitatively determined by a “spot test” using *p*-dimethylaminoazophenylarsonic acid in hydrochloric acid (1-2N) in the presence of hydrogen peroxide. It gives a brown precipitate. For differentiation between hafnium and zirconium, rufigallic acid in hydrochloric acid solution is used. Zirconium produces a deep purple colour, while hafnium has a light pink precipitate [13].

The most common quantitative method for determining zirconium is a gravimetric method involving ignition to zirconia after precipitation with mandelic acid, or ignition to ZrP_2O_7 after precipitation with phosphate ions. However, these precipitants are not specific for zirconium, leading to a determination of zirconium plus hafnium. There are a number of inorganic (approximately 10) and organic (around 42) precipitants that can be used in the gravimetric determination of zirconium [12, 15].

Volumetrically, zirconium is determined by a complexometric method using EDTA at pH 2.0, back-titrating with bismuth (III) and thiourea as indicator [13, 15]. In air samples, plasma emission spectroscopy is used [12].

Colorimetric methods are used to determine zirconium plus hafnium. Commonly, these methods include a separation step, such as solvent extraction. Three reagents are employed, namely 8-hydroxyquinoline, alizarin red S and catechol violet [15].

For the determination of hafnium in zirconium atomic absorption spectroscopy, mass spectrography, X-ray fluorescence spectroscopy and neutron activation methods can be used [12].

Impurities in zirconium and zirconium compounds are determined by emission spectroscopy, with arc-spark or plasma excitation. Atomic absorption spectroscopy can also be used. Sulphur and carbon in zirconium are measured by combustion, followed by chromatographic or infrared determination of the oxides. Hydrogen is determined by thermal conductivity after hot vacuum extraction, or by fusion of zirconium with a transition metal in an inert atmosphere and subsequent separation by gas chromatography. For oxygen and nitrogen, the fusion is carried out in the presence of carbon. Phosphorus is determined by visible spectroscopy using molybdenum blue. The more rapid method includes phosphine evaluation or a flame emission technique. Chlorine in low levels is determined by silver precipitation and silver by X-ray or atomic absorption spectroscopy. High levels of chlorine and fluorides are determined by using selective ion electrodes [12].

3 APPLICATIONS OF ZIRCONIUM

Zirconium and zirconium chemicals are applied in very different fields. About 95% of all the zirconium consumed is in form of zircon, zirconia and zirconium chemicals [25]. It is applied, among others, in ceramics (10%), in foundry sands (47%), as refractories (22%), in the construction of chemical plants, in electronic devices, in medicine and in nuclear reactors [13, 16].

Zirconium chemicals and zirconia in particular have recently attracted special attention as high-technology materials for multi-industrial and scientific applications because of their superior mechanical, thermal, electrical, chemical and optical properties.

3.1 Zirconium Metal

Zirconium free of hafnium (i.e. almost free) is produced for application in alloys containing low levels of tin or niobium, and used for structural parts in the core of water-moderated nuclear reactors. In this application zirconium has an amazing combination of characteristics, being ductile and having good strength up to 450 °C, which means that it can be formed and it does not deform in reactor conditions. In these alloys, it also shows very good corrosion resistance to pure hot water and steam. Another property of zirconium metal is its low thermal neutron cross-section absorption and this is the reason that it can be used in nuclear reactors as a container material for uranium oxide fuel pellets [7, 12, 13, 15].

Zirconium is also used in the construction of chemical reactors when corrosion resistance is required. Zirconium equipment can be used in hot sulphuric acid up to a concentration of 65%. It is used in the construction of hydrogen peroxide plants, in acrylic films and fibres, in methyl methacrylate, in butyl alcohol, in the production of urea, acetic and formic acids, and in nitric acid cooler-condensers [2, 12, 13].

Zirconium foil is used in ignition-flash material in photography bulbs. However, this application is falling away due to the use of electronic devices in new cameras. Zirconium powder is still in use in pyrophoric applications [12]. In combination with nickel, it is applied in pyrotechnic and ordnance areas, as a delay mixture and as igniters in squibs. Sponge zirconium finds its main use in the military industry [7].

Zirconium and its alloys with aluminium, iron, titanium or vanadium are used in vacuum tubes, in inert gas tubes and in ultra-high-purity environments in the semiconductor industry. This is possible because heated zirconium is able to absorb (reversibly) traces of hydrogen, oxygen, nitrogen, carbon monoxide and dioxide, and, irreversibly water. When these gases are adsorbed, they diffuse in the bulk of the material, leaving a fresh surface for new absorption [12].

Zirconium is used in satellites as a reflective surface agent, in superconductive magnets, in powder form (alloyed with lead) in cigarette lighter flints, and in metal-to-glass seals. It is also used in special welding fluxes due to its special properties. Furthermore, it is an ingredient in explosives mixtures [7].

Zirconium metal powders are a source of heat for squibs and ignition devices for a variety of uses, including automotive airbag inflators [7].

Zirconium has been injected intravenously as a prophylactic action to prevent the skeletal deposition of certain radioactive elements, especially plutonium [26].

Despite this long list of applications for pure zirconium metal, the consumption of zirconium ores for the production of pure zirconium metal represents only about 4% of the total use of the ores. The USA is the largest producer of zirconium metal, followed by France and the Ukraine [12].

3.2 Zirconium Chemicals in the Ceramic Industry

In this field, the most important zirconium chemicals are zircon and zirconia. Zircon is used in the production of refractory bricks and cements. Due to its high refractive index, zircon is used extensively as an opacifier in glazes and enamels. Its high refractive index gives a white, opaque appearance to the glazes and enamels. Zircon is also used in the production of alkali-resistant glass [2, 12].

Zirconia is important in the ceramic industry where it is mainly applied in the production of pigments. Zirconia and silica are fired together to produce zirconium silicate in the presence of small amounts of other elements. These elements enter the zircon lattice, forming different colours. The pigments are used in ceramic tiles, sanitary wear and metallic dishes. Zirconia colours are suitable for this application due to their resistance to high temperatures and to attack by molten glasses in glazes and enamels [12, 15].

3.3 Zirconium Chemicals in the Glass Industry

In the glass industry, zirconium chemicals are applied to increase the refractive index in optical glasses and for glass toughening. Zirconia and zirconium hydroxide are added for these purposes. Finely divided zirconium oxide is also used for polishing glass [7, 15].

Zirconium oxide and zirconium silicate are used as zirconium-containing refractories in glass-melting furnaces. The addition of zirconium oxide in these refractories increases thermal shock resistance [26].

3.4 Zirconium Chemicals in Electronic Devices

Zirconium hydroxide, zirconium acetate and zirconium propionate are used in electro ceramics and other special ceramics. These chemicals are used as dielectrics in capacitors, sensors and piezoelectrics. Zirconia is also applied for these purposes [7, 27].

Piezoelectric devices convert mechanical energy into electricity and vice versa. In this application, zirconia is combined with lead oxide in order to form lead zirconate. Another application is in ceramic sensors where zirconia is used for sensing oxygen, due to its capacity to absorb oxygen reversibly [27].

3.5 Zirconium Chemicals in other Fields

Zirconium hydroxide, acetate, propionate, oxychloride, hydroxycloride, nitrate, phosphate and orthosulphate, and ammonium zirconium carbonate are used in catalysis as supports and controllers. In this application, zirconium chemicals play a role mainly in four different areas [7]:

- In *autocatalysis,* zirconium chemicals are used to enable catalysts to operate at high temperatures and to displace oxygen.
- In *stationary catalysis,* zirconium chemicals enable specific reactions to occur.

- In *refinery catalysis,* they are used in refining reactions.
- In *chemical catalysis,* zirconia is applied as a precursor to other chemicals.

Examples of these applications can be found in polymer processing, where zirconium-based systems are applied in various processes of polymerisation. They are applied as homogeneous and heterogeneous catalysts for polypropylene, polyethylene and other polymers [7].

They can be used as a support for selective or complete oxidation systems of reaction, in hydrogenation as a promoter in fat/oil catalysis and as a support for nickel in general-purpose catalysts [7].

Zirconium chemicals in automotive catalysts improve the thermal properties in the wash coat. The thermal resistance of stationary catalysts is also improved if zirconium chemicals are added [7].

In the paper industry, zirconium chemicals are added to strengthen the paper and to enhance the resistance of the surface coating to water. As adhesives, zirconium chemicals promote greater adhesion of the ink to plastics and metals. Ammonium zirconium carbonate, zirconium acetate and zirconium propionate are applied for this purpose [7].

Hydroxide, acetate, propionate, phosphate and ammonium zirconium are applied in ink, pigments and paints production. [7].

Oxychloride, hydroxychloride and nitrate zirconium chemicals are also applied in the textile industry [7]. They are added to coating surfaces to give waterproof and flameproof properties to these surfaces [5, 11].

Zirconium oxychloride has been used as an antiperspirant. Zirconium carbonate and oxide are used to treat dermatitis [26].

Zirconium diboride (ZrB_2) is a potential material for high-temperature and high-wear oxidation- and corrosion-resistant applications. Some crystals are classified as gemstones and are then used in jewellery [5, 11].

4 ZIRCONIUM MINERALS

Zirconium does not occur as a free element in nature due to its high reactivity. It occurs as zirconium oxide, baddeleyite and other more complex oxides [2, 6]. In terms of abundance, it is the 9th metal in the Earth's crust and the 18th element, with an abundance of 0.016 - 0.025% [2, 5, 16]. Zirconium is found in crystalline rocks such as chlorites, schist, gneiss, syenite, granite, iron ore beds, sandstone and ferruginous sands [1, 2, 3, 5]. Zirconium is also found in abundance in stars and has been identified in the sun and in meteorites. Lunar rock samples also show high levels of zirconium oxide in comparison with terrestrial rocks [7].

More than 40 zirconium minerals are known. These minerals can be placed into five groups [12, 28]:

1. *Zirconium orthosilicates*: included in this class are zircon and its metamict[2] varieties
2. *Zirconium dioxide*: baddeleyite and its altered varieties[3]
3. *Zircon silicates with sodium, calcium, iron and other elements*: the most important *zircon silicate* is eudialyte; eucolite, genttinsite and others are included
4. *Zirconium carbonates with sodium, calcium and other elements*: weloganite and others
5. *Others*: including zirconolite ($CaZrTi_2O_7$).

Among the high number of zirconium sources, zircon and baddeleyite are the most important. Zircon and baddeleyite contain varying amounts of radioactive U^{238} and Th^{232}, as impurities. The concentration of U and Th is 300 - 500 ppm in zircon and up to 1 000 ppm in baddeleyite [6]. Zircon is the predominant source of commercial zirconium minerals. It occurs in beach and river sands with other heavy minerals. Baddeleyite and eudialyte are also used. They are all obtained as by-products in the recovery of other minerals, such as rutile, ilmenite, monazite and garnet in river and beach sands [1, 2, 12].

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[2] Radiation damage occurs in zircon with U and Th as impurities owing to the radioactive decay of the latter

[3] Owing to U and Th radiation.

4.1 Zircon

Zircon is a naturally occurring zirconium silicate. It occurs in silica igneous rocks, particularly in granite, nepheline syenite and pegmatite. In metamorphic and sedimentary rocks, it occurs as an accessory mineral [2, 3, 12]. Zircon is found concentrated with other heavy minerals, such as rutile, ilmenite, monazite, leucoxene and garnet in river and beach sands. This is due to the high specific gravity of zircon, 4.6 - 4.8. In these deposits, iron and titanium appear to be the main contaminants [2, 3, 5, 14, 16]. Separation is effected through electrostatic, magnetic and gravitational techniques, through which levels of 99% purity can be achieved [2, 12].

Zircon sand is yellow in colour. Sometimes beautiful, crystal clear or vividly coloured zircon crystals are found, which are used as gems. Crystal clear zircon resembles diamond. Blue-green dichroitic zircons from Vietnam and topaz-coloured “hyacinth” stones from Ceylon are used as gemstones [5]. The variety of colours ranges from yellow, brown to red and the zircons may be colourless, green, rose-red, or violet [11]. Their appearance can be attributed, in part, to radioactive action [29].

Zircon is mined as a co-product of rutile, ilmenite and monazite. The mining of zircon and other heavy minerals is environmentally friendly. It involves the removal of light sands and mining is done with elevating scrapers and bulldozers. As heavy sands constitute only 4 - 7% of the whole deposit, the replacement of light sands can restore the original elevation of the sand and so the vegetation can be replaced [1, 3, 12]. Zircon extraction involves three stages – mining, wet concentration and dry separation [1].

The wet concentration process consists of two steps. In the first step, the raw material is subjected to magnetic separation. This process allows the separation of iron compounds. In the second step, the other contaminants are removed via solubility in hot sulphuric acid. It is preferable to grind the raw material beforehand [5].

4.1.1 Structure and properties of zircon

Zircon has a tetragonal structure, consisting of a chain of alternating, edge-sharing SiO_4 tetrahedra and ZrO_8 bisdisphenoids, also known as triangular dodecahedra or dodecadeltahedra. The bisdisphenoids have 8 vertices, 18 edges and 12 faces. This polyhedron consists of two interpenetrating, concentric tetrahedra [3, 8, 9, 10, 12, 15, 17, 30]. The name is derived from the fact that the structure consists of a sphenoid that has a wedge. A disphenoid is a tetrahedron with triangular faces [6, 17].

Zirconium and silicon atoms are linked by oxygen atoms. Although zircon has been formulated as $ZrSiO_4$ or $ZrO_2.SiO_2$, X-ray studies do not show significant differences between the oxygen atoms in the structure. This leads one to the conclusion that there are no separate groups of oxygen atoms and therefore the structure $ZrSiO_4$ is adequate. However, there is a remarkable formation of complex tetrahedron anions, $Si(O)_4$, surrounding zirconium cations. Another explanation that could justify the second formulation, $ZrO_2.SiO_2$, is the fact that at high temperatures the compound appears to be separated into two parts, ZrO_2 and SiO_2. In addition, with magnesia at 1 240°C zircon is completely converted to magnesium silicate and zirconia [5]. Figure 4.1 shows an atomic model of the structure of zircon crystals and Figure 4.2 a geometric design of zircon crystals. The green polyhedra represent the ZrO_8 bisdisphenoid structure and the SiO_4 tetrahedron is shown in blue.

The density of zircon varies according to its origin. Some authors have attributed these differences to the presence of an unknown component in the matrix. The density of zircon may be as low as 3.95 g/cm^3, but after beneficiation it is closer to 4.6 g/cm^3 on average. Light zircons contain free amorphous silica and amorphous zirconia. This transformation is attributed to radiation damage caused by α-rays. Heating restores the proper density [5].

The zirconium tetravalent ion in this compound is highly coordinated (8). Due to its structure, zircon is a very stable compound, both chemically and thermally [3, 4, 16, 31]. Zircon decomposes to ZrO_2 and SiO_2 under atmospheric conditions only above 1 690 °C [30]. This can also be achieved via plasma at high temperatures [3, 30].

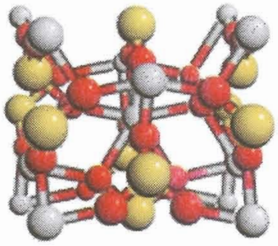

Figure 4.1: Atomic model of structure of zircon crystals

In general, zircon is unreactive to strong mineral acids, but is attacked by concentrated sulphuric acid at high temperature and pressure. Fluorides, such as hydrogen fluoride, potassium bifluoride and others, can convert zircon into complex zirconium fluoride and silica. Chlorination at high temperature in the presence of carbon gives zirconium tetrachloride [13]. Zircon's extreme stability with respect to strong mineral acids is the basis of the purification of zircon from various contaminants in its ores [5].

Finely divided zircon can be easily decomposed by fused alkali or alkali carbonates at their melting temperatures to orthosilicates and orthozirconates or metal zirconium silicates. At high temperatures, alkaline-earth metal oxides also react with zircon, giving the same products [5, 13].

The main producing countries are Australia, India, the USA and South Africa. World production in 1987 was about 800 000 tons per annum, with 55% coming from Australia [32].

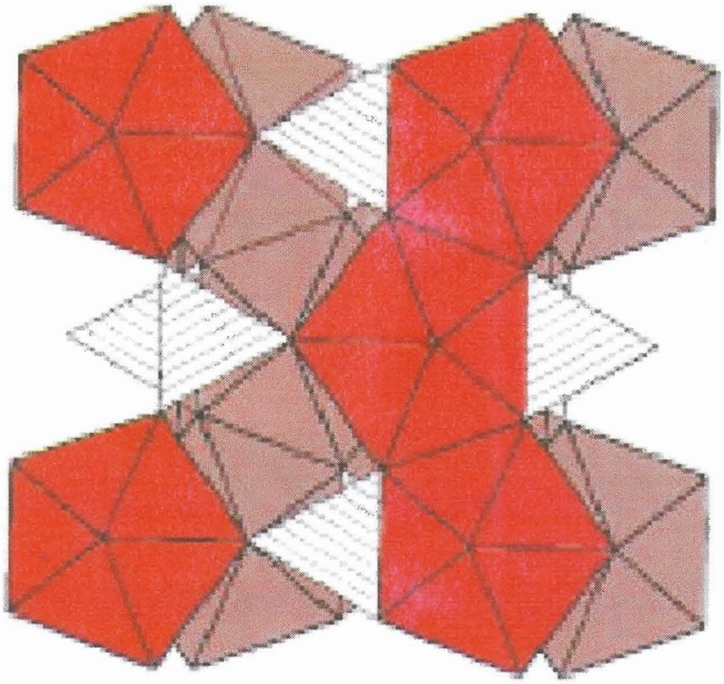

Figure 4.2: A geometric design of zircon crystals. The red polyhedra represent the ZrO_8 bisdisphenoid structure and shown in brown is the SiO_4 tetrahedron.

4.1.2 Some applications of zircon

Zircon on its own has a considerable number of applications, the most important being applications in foundries, refractory ceramics and as opacifiers.

a. Zircon as opacifier

Opacifiers are an important market for zircon in the ceramic industry. Zircon imparts high opacity and extreme whiteness to the glaze. It also improves colour stability and assists in the development of desirable properties on the fired glaze surface. Typically, zircon glaze uses 8 - 12% of milled zircon, depending on the degree of opacity required [33].

White pigments are widely used in ceramic glazes and enamels. The most powerful white pigment is titania. However, zircon is commonly used as an opacifier in the decorative ceramic industry, in tile glazes, and in porcelains and enamels [12, 16, 34, 35] owing to its higher thermal stability.

A black or white appearance depends on the behaviour of the matrix to incoming light. If the object absorbs all, or almost all, the incident light, then the object will appear to be black and opaque. A white object reflects most of the incoming beam, which enter the viewer's eye, giving a white shade [35].

Opacity is governed chiefly by the relative refractive indices of crystals and their media. Zircon has a high refractive index (1.92). Other factors that affect the quality of opacifiers are related to the number of independent light scatterers, and the size and shape of the particle crystals [34, 35].

To be used as an opacifier, zircon must be of a chemically high grade (ZrO_2+HfO_2>66%), with minimal amounts of iron (less than 0.05%) and titania (less than 0.1%). The grain size must be between 5 - 9 μ [33].

b. Zircon in refractories

Zircon is used as a refractory material in the glass and steel industries [12, 16]. In the glass industry, it can be used in association with alumina, which has high corrosion-resistance to molten glass. This is due to the low solubility of zirconium in molten silica [16, 33]. This corrosion resistance, the low defect potential and good manufacturing ability makes zircon-based refractories particularly suitable for the most exposed hot areas of a furnace [33]. In the steel industry, zircon is used in ladles and continuous casting nozzles [12].

Zircon is used fused or combined with alumina. This material has high resistance to corrosion by molten glass. The ceramic material has been used in contact zones, e.g. the sidewalls of glass smelters and refiners, and in furnaces [7, 12, 16, 33].

Zirconium silicate absorbs X-rays. For this reason it is added to glass television tubes to absorb the outgoing X-rays. It also toughens the glass [7, 12, 16].

c. Zircon in foundries

Zircon is used in foundries as the basic mould or as a facing for other mould materials, especially when high refractoriness is required to prevent metal penetration into the fused sand. This is the third most important market for zircon [33].

Nielsen and Chang [12] attributed zircon's usefulness in this application to its high thermal conductivity that allows higher cooling rates than other mould materials, as well as to zircon's high melting point and chemical stability.

In precision casting, zircon "flour" is used as a refractory paint in mouldings to provide heat resistance and reduce metal penetration into the mould [12, 33]. This is related to zircon's high melting point, low coefficient of thermal expansion and chemical stability.

The materials used in a foundry have an important impact on the production costs. Hence, the use of zircon sands in foundries is affected by the market prices of zircon. When prices are high, alternatives such as chromite, olivine and aluminosilicates are used [33].

4.2 Zirconia

Zirconia occurs naturally in monoclinic form as baddeleyite (also known as brazilite, zirkite or caldasite). The first deposit of relatively pure zirconia was discovered in Brazil by Hussak in 1892. E. Ritz was the first to exploit this deposit commercially [5, 13, 16, 36, 37]. According to Ryskewitch and Riecherson [5], the name "baddeleyite" was given to zirconia by L. Fletcher who discovered it before Hussak in samples from Ceylon. Joseph Baddeley collected the samples in which Fletcher found zirconia, in Sri Lanka, hence the name [37].

The average content of zirconia in baddeleyite is 80%. Some sources yield baddeleyite with 90% or more of zirconia [5, 13]. Ores of this kind can be used immediately in many applications without pre-treatment. The major problem with natural sources of baddeleyite is that they are scarce and are limited in terms of availability.

There are various deposits of baddeleyite in different countries, but their commercial importance depends on the purity of the deposits. Their radioactivity is an important factor in the quality of the deposits. Crude forms of baddeleyite are found in Brazil and Sri Lanka. The main commercial sources are found in the Kola Peninsula in Russia and in Phalaborwa, South Africa [15, 16, 32, 37].

Baddeleyite is beneficiated by the gravity separation of heavy minerals. Thereafter, the product is acid-leached and magnetically separated to obtain a commercial-grade product containing 96% to 99.5% of ZrO_2+HfO_2. The product typically contains HfO_2 at levels of 1.5-1.7% [37].

Baddeleyite occurs with forsterite, apatite and magnetite. In these zones, baddeleyite may constitute up to 0.15% [38].

Although the production of baddeleyite is confined to South Africa and Russia, much zirconia is produced in many countries, from zircon sands. In 1995, 31 000 tons were produced worldwide, with South Africa producing 18 000 tonnes [39].

4.2.1 Properties of zirconia

Zirconia is the most stable oxide of zirconium. Zirconium oxide is a high refractory material. In its pure form it is a white powder with a melting point of 2 710 ± 35 °C. Stabilised zirconia has a lower melting point, and with 15% of calcia or magnesia it can melt at 2 500 °C. The boiling point is calculated to be approximately 3 730 °C, using values of the vapour pressure of zirconia [5, 33].

Zirconia is hard, strong and chemically inert, with a high melting point, a low coefficient of friction and low specific heat. It is an excellent thermal insulator and is biocompatible [32]. As a result of its intrinsic proprieties, zirconia is a most important zirconium chemical. It is applied in various fields of science and technology.

Zirconia is polymorphic. It exists in three crystalline forms: monoclinic, which is the stable form up to 1 170 °C; tetragonal, which is stable between 1 170 °C and 2 370 °C; and cubic, which is stable above 2 370 °C [4, 38]. Cubic zirconia is widely used as a diamond substitute for decorative and industrial applications [4, 5]. Collins established that the cubic structure of zirconia is of the fluorite type. Ruff and collaborators established the nature of these modifications (Figure 4.3) [5].

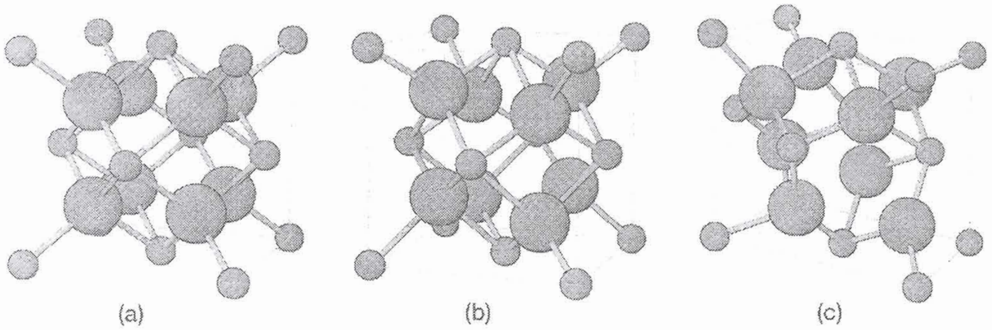

Figure 4.3: Schematic representation of polymorphic forms of zirconia: (a) cubic, (b) tetragonal, and (c) monoclinic

The transformation of the monoclinic structure to the tetragonal structure is followed by a volume contraction of about 9%. In fact, the monoclinic form has an average density of 5.31 while that of the tetragonal modification is 5.72, and that of the cubic modification is 6.09 [5].

The volume contraction makes it difficult to produce ceramic pieces by firing zirconia directly. The phase transformation can be avoided by adding small amounts of other oxides forming a solid solution with zirconia. These oxides must have a cubic structure. They cause a slight stress in the zirconia lattice, forcing it to retain the cubic structure on cooling. The discovery of the way to control this transformation had a pivotal effect on zirconia applications [40]. The atomic radius of the oxides must be of approximately the same in order to make it possible for them to enter into the zirconia lattice structure. Those solutions have important properties: at low temperatures they are good insulators and above 900 °C they exhibit high electrical conductivity. These properties can be considered the antecedent to incandescent light [5].

Zirconia is a typical amphoteric oxide: it acts as a base with strong mineral acids and as an acid with strong bases. In both cases it forms comparatively stable salts. Generally, salts with strong acids and hydrofluoric acid are soluble in water. Solutions of zirconium salts diluted in water can suffer from hydrolysis, forming hydroxy or oxy salts. That can be shown by zirconium chloride [5, 13]:

$$ZrCl_4 + H_2O \rightarrow ZrOCl_{2\,(aq)} + 2HCl$$

$$ZrOCl_{2\,(aq)} \rightarrow Zr(OH)OCl_{(aq)} + HCl, \text{ etc.}$$

Scheme 4.1: Hydrolysis reaction of zirconium tetrachloride in water [5, 13]

Zirconia is soluble in alkali melts, such as sodium or potassium, forming alkali-meta-zirconates. It is not reducible by alkali metals under normal conditions, but is reducible at the high temperatures at which those metals become volatile. With alkaline earth metals, including beryllium and magnesium, zirconia reacts at elevated temperatures, resulting in the reduction of zirconia to metal. Aluminium can also reduce zirconia. Silicone can reduce zirconia only at temperatures above 1 800-°C. Zirconia reacts with carbon at 1 250 – 1 300 °C to form zirconium carbide, bypassing metallic zirconium [5].

Zirconia has an impressive combination of properties, including great hardness, high strength, a high melting point and biocompatibility. In association with calcia, magnesia, yttria and rare earth oxides, zirconia[4] competes with metals and alloys in some applications, especially where

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[4] Stabilised zirconia, by doping with these oxides.

high-temperature performance, and resistance to erosion and corrosion are required [4, 31, 38, 40].

Zircon, as stated, is the major and cheaper source of zirconia and is very stable, both chemically and thermally. To extract zirconia from zircon requires aggressive chemical and thermal conditions, or very high temperatures to break the bonds between the two oxides (ZrO_2 and SiO_2). Several methods of producing zirconia from zircon sands have been investigated [3, 4].

4.2.2 Applications of zirconia

Most of the applications of zirconia are associated with its high chemical and thermal stability. Zirconia is applied to the surface of other materials, in refractories, as a coating for structural ceramic materials to provide thermal and corrosive protection. The nozzles and inner surfaces of wall furnaces can have zirconia coatings. Zirconia can be used to replace fireclay and similar aluminosilicates if they are unable to achieve the required refractoriness or corrosion stability [12].

Zirconia is a ceramic material and ceramic materials have been called "the material of the future" since they are derived from sand. Sand composes about 25% of the Earth's crust. In comparison, all metals together compose only 1% of the Earth's crust. For our purpose, a ceramic material can be defined as a non-metallic and inorganic material and, in most case; these materials have been treated at high temperature during their manufacture [11].

a. Zirconia in paints and pigments

Zirconia is used in the paint industry to coat the surface of titania pigment particles for specific exterior paint applications. It minimises ultraviolet excitation of the titanium atoms, which would otherwise react with the organic binders in the paint and thus reduce the lifetime of the paint [12].

Zirconia is also used to replace titania as a pigment in the camouflage paints used in snow environments because it more closely camouflages snow in the infrared and microwave spectra [12].

Zirconia is used as a pigment for stoneware in the ceramic industry. (Stoneware is high-fired, coarse vitreous clay ware.) Such pigments are inexpensive and have low toxicity. In these industries an estimated 6 000 tons of zirconia are used per year [16].

b. Zirconia in jewellery

Single crystals of zirconia with a cubic structure are used in jewellery as low-cost gemstones. For this application, more than 300 tons of single crystals are grown every year worldwide [7, 12].

Cubic zirconium dioxide is a synthetic stone used as diamond simulant. It can be given different colours, depending on the dopants applied in cubic zirconia production. The dopants are used to induce cubic crystallisation. Well known among zirconia gemstones is the so-called white zirconia, a colourless modification of zirconia. With cerium, red, orange and yellow gems can be obtained. Yellow, amber and brown gems are obtained with copper, iron, nickel, praseodymium and titanium oxides. Erbium, europium and holmium oxides produce pink gems. Chromium, thulium and vanadium oxides produce olive green, while cobalt, manganese and neodymium oxides produce lilac and violet gemstones. Other colours such as sapphire blue and emerald green can be produced under specific conditions [41].

c. Zirconia in electronics

Stabilised zirconia (SZ) is used as a solid electrolyte at elevated temperatures in oxygen sensors and high-temperature fuel cells. This is due to the voids in the lattice structure that allow oxygen ions to diffuse through them at high temperatures. At room temperature, stabilised zirconia is an insulator. Some kinds of stabilised zirconia are used in resistors and susceptors. Yttria-stabilised zirconia cylinders, inductively heated, are used as heat sources to melt quartz bowls for the drawing of quartz optical fibres [12].

Zirconia is used in oxygen-sensing devices. The electrochemical cell is made in such a way that one side has a known fugacity and the other the unknown fugacity. When the oxygen is adsorbed at that surface of the sensor, a drop in the electrochemical potential develops and a voltage is generated. This voltage is related to the fugacity [27].

Zirconia can replace titanium in lead titanate, forming a solid solution that has piezoelectric properties. The desired composition is 53:47 (Zr:Ti). Lead titanate and lead zirconate (PZT) solution doped shows electro-optical properties. PZT piezoelectric ceramics are used in gas furnaces and barbeque igniters, microphones, phonograph crystals, in ultrasonic transducers for agitation in cleaning tanks and in underwater sonar. Lanthanum is one of the dopants that produce material with good electro-optical properties and high optical transparency. This class of materials is called PLZT (lead lanthanum zirconate titanate). A useful composition is a Zr:Ti ratio of 65:35 and 8 - 9% mol of lanthanum [12, 27].

d. Zirconia in the medical field

Nowadays, ceramic materials are competing with the common metal-polyethylene or metal-metal joint prosthesis devices in orthopaedic surgery, because they reduce strongly the amount of wear debris [11, 42]. Ceramic materials present excellent biocompatibility. They have high mechanical resistance, high wetability and high stability [11].

Alumina was very popular in this field in the 1980s. It was used in hip joints in femoral ball heads. Although alumina is chemically more stable than zirconia, critical fracture problems led to its falling into disuse. Zirconia is twice as strong and mechanically harder than alumina. For this reason, zirconia has been used as a replacement for alumina to solve the critical fracture problem. In this use, zirconia shows high biocompatibility and high resistance to scratching [11, 43, 44]. Phase transformation in zirconia ceramics may, however, cause fracture and roughness in the surface of prostheses [45].

Zirconia is used in the treatment of dermatitis [26]. Zirconia lead oxide and titania are used in the piezoelectric ceramic systems that are used in ultrasonic transducers for medical ultrasound imaging [12].

e. Zirconia in other applications

In its stabilised form, zirconia is used in fishing rods, ferrules, knives, unbreakable shirt buttons and golf putter heads [12].

Partially stabilised zirconia ceramics are considered to be advanced ceramics and as such have been commercialised since 1970. According to the amounts of stabilising agent added, these zirconia ceramics exhibit different properties in response to stress under different loading conditions. They are applied in wiredrawing technology, for thermal shock conditions, in combustion engines (cylinder lines), valve seats and bypass valve guides [16].

Zirconia is used in ceramic oxygen generators (COGs). A COG is an electrochemical device that employs an oxygen-ion-conducting electrolyte, such as stabilised zirconia, to generate oxygen electrochemically from air and other gases, such as carbon dioxide and water vapour. This technology is under consideration for use on Mars [46].

5. RECOVERY OF ZIRCONIA FROM ZIRCON SANDS

The use of zirconia in many fields has grown enormously. The major and cheapest source of zirconia is zircon sand. Despite this, the decomposition of zircon is not easy to achieve due to its stability. Considering the structure of zircon, which is extensively discussed in the literature [3, 9, 10, 16, 47], this stability is quite understandable. Various methods of decomposition have been investigated owing to the different levels of purity required and the cost of manufacture. All these methods have three steps in common. Firstly, zircon is decomposed or dissociated by chemical, thermal or mechanochemical means. Secondly, the products obtained are treated by solubility differentiation. Thirdly, the zirconium compounds are isolated from the residual impurities.

5.1 Thermal Dissociation

The reaction is conducted in an arc plasma furnace that forms zirconia in droplets of silica. To avoid recombination or to reduce it to minimum levels, the mixture must be quenched rapidly. As a result, it produces crystals of zirconium oxide in amorphous silica. Further leaching with sulphuric acid is necessary to produce a zirconium sulphate solution and insoluble silica [12]. For leaching, sodium hydroxide can also be used. In this case, aqueous sodium silicate and zirconia are obtained. Sodium silicate is a useful by-product, which therefore can be commercialised. This process is environmentally friendly [2, 12].

In other processes, zircon is decomposed in an arc furnace at 2 000 °C. Silicone monoxide is generated, which re-oxidises to silicone dioxide outside the furnace [2, 16].

5.2 Decomposition by Fusion

The fusion procedure is very common in the recovery of zirconia from zircon sands. In this procedure, different fondants can be used. These include sodium hydroxide, sodium carbonate and calcium carbonate [12].

5.2.1 Fusion with sodium hydroxide

This is the well-known and usual method. Fusion is conducted at 650 °C with a slight excess of sodium hydroxide. In the formal process, the products of fusion obtained are sodium zirconate and sodium metasilicate or orthosilicate, depending on the mol ratios of alkali. The cooled reaction products are crushed and leached with water. As a result, sodium metasilicate is dissolved and sodium zirconate is hydrolysed to hydrous zirconia. Hydrous zirconia is insoluble and is recovered by filtration [2, 12, 15, 48].

$$\mathrm{ZrSiO_4 + 4NaOH \rightarrow Na_2ZrO_3 + Na_2SiO_3 + 2\ H_2O}$$
$$\mathrm{ZrSiO_4 + 6NaOH \rightarrow Na_2ZrO_3 + Na_4SiO_4 + 3\ H_2O}$$

Scheme 5.1: Reaction of zircon decomposition with sodium hydroxide by fusion, with high stoichiometric ratios [2]

$$\mathrm{Na_2ZrO_3} + x\mathrm{H_2O} \rightarrow NaOH_{(aq)} + ZrO_2.x\mathrm{H_2O}$$

Scheme 5.2: Reaction of hydrolyses of sodium zirconate

Recovered hydrous zirconia is fired and dissolved in mineral acids, which leads to the formation of various aqueous zirconium compounds that differ according to the mineral acid used [2, 12, 15, 48].

If the fusion is conducted with an insufficient amount of sodium hydroxide, sodium zirconium silicate is obtained as a major product.

$$\mathrm{ZrSiO_4 + 2NaOH \rightarrow Na_2ZrSiO_5 + H_2O}$$

Scheme 5.3: Reaction of zircon decomposition with sodium hydroxide by fusion, with low quantities of sodium hydroxide [2]

Na_2ZrSiO_5 is insoluble in water and therefore requires acid treatment to dissolve the cake [2, 12, 48].

5.2.2 Fusion with sodium carbonate

For this fusion, temperatures must be higher than 1 000 °C. In contrast to sodium hydroxide fusion, the compound of zirconium obtained is sodium zirconium silicate, which is water-insoluble, being soluble only in acid. Strong acids therefore have to be used to dissolve it. The common process uses hydrochloric acid [12].

$$ZrSiO_4 + Na_2CO_3 \xrightarrow{1000^\circ C} Na_2ZrSiO_5 + CO_2$$

$$Na_2ZrSiO_5 + 4HCl \longrightarrow 2NaCl + ZrOCl_2 + SiO_2 + 2H_2O$$

Scheme 5.4: Reaction of zircon decomposition using sodium carbonate as fondant, with subsequent treatment with hydrochloric acid [2]

At high ratios of sodium carbonate, sodium zirconate and sodium silicate are also formed. This can be explained by the following reaction equation [2]:

$$Na_2ZrSiO_5 + Na_2CO_3 \rightarrow Na_2ZrO_3 + Na_2SiO_3 + CO_2$$

Scheme 5.5: Reaction of zircon decomposition using sodium carbonate as fondant, with low amount of sodium carbonate [2]

5.2.3 Fusion with calcium oxide and magnesium oxide

With calcium oxide, calcium zirconium silicate, calcium zirconate and calcium silicate are produced. A mixture of zirconium dioxide and calcium or magnesium silicate can also be produced. The products are dependent on the mol ratio of the reactants and on the temperature of the process [2, 49].

$$ZrSiO_4 + CaO \xrightarrow{1100^\circ C} Ca_2ZrSiO_5$$

$$ZrSiO_4 + 2CaO \xrightarrow{1600^\circ C} Ca_2SiO_4 + ZrO_2$$

Scheme 5.6: Reaction of zircon decomposition with calcium oxide, with two different mol ratios [2, 49]

Magnesium oxide is the most suitable fondant for the reaction using the alkaline earth oxides, because of its high solubility and its almost negligible rates of hydration and carbonation. It is available in nature in the form of the mineral periclase [49].

5.2.4 Fusion with potassium fluorosilicate

The mixture of potassium hexafluorosilicate and zircon is fused at 700 °C and potassium hexafluorozirconate is obtained. The resulting mass is crushed, and then the fluoride salt is dissolved with acidified hot water. Filtration of the solution removes the silica and further cooling of the filtrate leads to the crystallisation of potassium hexafluorozirconate [2, 12, 16].

$$K_2SiF_6 + ZrSiO_4 \xrightarrow{600-700^{\circ}C} K_2ZrF_6 + 2SiO_2$$

Scheme 5.7: Reaction of zircon decomposition using potassium hexafluorosilicate as fondant [2, 16]

The product is milled and leached with a 1% hydrochloric acid solution at about 85°C for two hours. The saturated solution is filtered while hot to remove the silica, and potassium hexafluorozirconate crystallises as the solution cools [15, 16].

Potassium hexafluorosilicate is preferred to sodium hexafluorosilicate because of a lower tendency to dissociate and form silicon tetrafluoride by sublimation. Potassium chloride or carbonate can be added to the fusion product to promote completion of the reaction; they also reduce the tendency to dissociation of the potassium compound [15].

5.2.5 Fusion with calcium carbonate (or lime)

Lime (calcium oxide) or dolomite (a mineral that is a mixture of calcium carbonate and magnesium carbonate) can be used as a fondant. The resulting products are calcium zirconate and calcium and/or magnesium silicate. During the cooling process, the mass disintegrates into a very fine powder and coarse crystals of calcium zirconate. This difference enables the two to be separated by mechanical means. Since calcium zirconate is acid-soluble, it can be converted into a number of different chemicals or into zirconia [12, 19].

$$2ZrSiO_4 + 5CaCO_3 \rightarrow 2CaZrO_3 + (CaO)_3(SiO_2)_2 + CO_2$$

$$ZrSiO_4 + CaO + MgO \rightarrow CaO.MgO.SiO_2 + ZrO_2$$

Scheme 5.8: Reaction of zircon decomposition using calcium carbonate and oxides of magnesium and calcium as fondants

The second process is used on an industrial scale, while the first does not seem to have been attracted any commercial interest [48].

5.3 Chlorination

American and French zirconium metal producers are using this process. Chlorine is used as a fluidising gas and the reaction is endothermic. The energy required for the process is supplied via induction heating of the internal graphite walls of the chlorinator. The reaction takes place at 1 100 °C. The gases produced, consisting of zirconium tetrachloride, silicon tetrachloride and carbon monoxide, are cooled down to 200 °C [2, 12, 15, 48].

$$ZrSiO_4 + 4Cl_2 + 4C \rightarrow ZrCl_4 + SiCl_4 + CO$$

Scheme 5.9: Reaction of zircon carbochlorination

During the first cooling, zirconium tetrachloride, containing hafnium as impurity, is collected as a powder. Silicon tetrachloride is condensed following further condensation and is subsequently purified and used to produce fumed silica, fused quartz and fused quartz optical fibre [2, 12]. Currently, milled zircon and coke are chlorinated in fluidised beds using chlorine as fluidising medium [12, 15, 16].

Zirconium tetrachloride can be converted to oxychloride with water. Zirconium oxychloride can be crystallised by cooling the solution to 20 °C. This step allows major impurities to be separated out. The crystals can then be calcined to zirconia [16].

5.4 Carbiding Process

The process is done in an arc furnace, with the furnace being continuously fed from the top. In order to obtain complete vaporisation of the silicon monoxide and complete conversion of zircon to carbide, an insufficient quantity of carbon is used. The process can be summarised by the following reaction [12]:

$$ZrSiO_4 + 3C \xrightarrow{2500^\circ C} Zr(C, N, O) + SiO + 3CO$$

Scheme 5.10: Reaction of the zircon carbiding process

Zirconium carbonitride crude grows under the electrode, surrounded by unreacted mix, which acts as insulation for the steel furnace shell. The zirconium-containing product can be roasted in air to give a low-purity zirconia for use in refractories [2, 12].

The advantage of the process is that it is completely dry. There is, however, an environmental concern related to the airborne silica produced during the process. The alternative treatment consists of the chlorination of zirconium cyanonitride to zirconium tetrachloride [2, 12, 15].

5.5 Other Methods of Recovering Zirconia

Due to the high demand for zirconium and zirconium chemicals, new methods of recovering zirconia from zircon sands have been proposed by scientists. The following methods of zirconia recovery were found in a literature search.

5.5.1 Fusion with calcium sulphate

This method was proposed by Hanna [50]. The method is based on the thermal decomposition of calcium sulphate to calcium oxide. Temperatures varying from 900 °C to 1 400 °C were used, with a soaking period from 30 minutes to 3 hours.

The advantage of using calcium sulphate is that it decomposes to CaO and SO_2. Sulphur dioxide can be used to produce sulphuric acid. It appears to be a good process for countries with large sources of gypsum, the mineral of calcium sulphate [50].

5.5.2 Mechanical zirconia processing

Zircon is milled for long periods (100 to 340 hours) in a ball mill, with alkaline earth metal oxides [49, 50, 51]. As result, zirconia is released and the silica reacts with the alkaline earth metal oxides, according to the following reaction scheme:

$$\mathrm{MO} + \mathrm{ZrSiO_4} \rightarrow \mathrm{MSiO_3} + \mathrm{ZrO_2} \qquad \text{(a)}$$

Scheme 5.11: Reaction scheme of the mechanical decomposition of zircon in the presence of alkaline earth metal oxides [49, 50, 51]

Here M represents the alkaline earth metals, namely magnesium, calcium, strontium and barium. The above scheme is consistent with a 1:1 mol ratio. When the ratio of alkaline earth metals is increased, parallel reactions occur:

$$MO + ZrO_2 \rightarrow MZrO_3 \quad (b)$$
$$MO + MSiO_3 \rightarrow M_2SiO_4 \quad (c)$$

Scheme 5.12: Mechanism of the mechanical decomposition reaction of zircon in the presence of alkaline earth metal oxides [49, 50, 51]

Reaction (a) is predicted to occur at 25°C. When magnesium is used, the free energies of (a) and (c) are similar, suggesting competition between the zircon and the metal metasilicate. A possible solution is to increase metal oxide amount to favour the formation of metal zirconates [51].

The hydroxide is less favourable than the oxides and the milling environment must be free of water. Although those reactions occur at room temperature, simply mixing zircon with these oxides does not produce any reaction. This can be explained either by negligible kinetic rates, related to the slow diffusion, or by the activation energy requirement [51].

Magnesium is the most appropriate alkaline metal oxide for this reaction because of its high solubility, and its low rates of hydration and carbonation [49].

5.5.3 Hydrothermal decomposition

The reaction is taken under autoclave conditions in aqueous media. Zircon is reacted with calcium hydroxide and sodium hydroxide. In the first stage, zircon reacts with sodium hydroxide according to following scheme of reaction:

$$ZrSiO_4 + 2NaOH \rightarrow Na_2ZrSiO_5 + H_2O$$
$$Na_2ZrSiO_5 + Ca(OH)_2 \rightarrow ZrO_2 + CaO.SiO_2.H_2O + 2NaOH$$

Scheme 5.13: Reaction scheme of zircon hydrothermal decomposition with calcium hydroxide in the presence of sodium hydroxide [52]

Sodium zirconium silicate reacts with calcium hydroxide to produce calcium silicate hydrates and zirconia, leaving unreacted sodium hydroxide, which plays a catalytic role in the reaction [52].

The resulting reaction includes only zircon and calcium hydroxide:

$$ZrSiO_4 + Ca(OH)_2 \rightarrow ZrO_2 + CaO.SiO_2.H_2O$$

Scheme 5.14: The overall reaction scheme of zircon hydrothermal decomposition with calcium hydroxide in the presence of sodium hydroxide [52]

The reaction is temperature-dependent. Increasing the reaction temperature has a positive effect on the reaction rate but above 100°C this also implies increased pressures [52].

The efficiency of the process reaches a maximum when the ratio of $Ca(OH)_2$:$ZrSiO_4$ equals 2 for a constant amount of sodium hydroxide. The size of the zircon particles influences the reaction strongly. The reaction is pH-dependent [52].

5.5.4 Anion-exchange process

Mohammed and Daher [53] proposed this decomposition process. Firstly sodium hydroxide is used to produce sodium zirconate and sodium silicate at 650°C. The cooled cake is leached with water and the wet residue digested in acid, filtered and washed in acid and then with demineralised water, and pH-adjusted. This solution was used for further experiments.

The zirconium solution is then passed through an anion-exchange resin to extract impurities of iron and uranium as complexes $[FeCl_4]^{2-}$ and $[UO_2Cl_4]^{2-}$. Zirconium is precipitated from the effluent as sulphate tetrahydrate. The sulphate is then calcined at 1 000 °C to zirconia [53]. The calcined residue consisted of high-purity zirconia.

5.6 Recovery of Zirconia from Baddeleyite

Although, on average, baddeleyite is composed of 80% by mass of zirconia, for certain applications complementary purification is needed. Several methods applied for baddeleyite purification are also used for zircon decomposition products.

5.6.1 Basic sulphate method

The US Bureau of Mines developed this method. It is based on the precipitation of zirconium basic sulphate. A constant acidity must be maintained during precipitation by dilution and the reaction temperature must be maintained at 39.5 °C. The acidity of the media increases due to the formation of free acid. If these conditions are met, then the yield can achieve values as high as 40% to 58%. The basic sulphate recovered in this way contains only traces of impurities [54].

The main difficulty in this process lies in controlling the acidity of the media as a result of the hydrolysis of zirconium sulphate with the formation of free sulphuric acid, according to the following reaction:

$$4Zr(SO_4)_2 + 19H_2O \rightarrow 4ZrO_2.3SO_3.14H_2O + 5H_2SO_4$$

Scheme 5.15: Reaction of the hydrolysis of zirconium sulphate in water during the processing of zirconium basic sulphate [54]

To overcome the problem, sulphuric acid is replaced by hydrochloric acid and soluble sulphates are added to provide sulphate ions. Sulphates of aluminium, sodium, magnesium and ammonium are used for this propose. With this alternative method, yields of around 97.5% can be achieved [54].

In another processing method, zirconyl sulphate solution is treated with sulphuric acid to give a mol ratio of zirconium to sulphate ions equal to 5:2. The solution is heated at 90 °C and diluted with water. At the same time, ammonium solution is added to keep the pH at 1.4. Basic zirconium sulphate, $Zr_5O_8(SO_4)_2.xH_2O$, is precipitated in over 99% yield. The precipitate is converted into hydroxide by refluxing with ammonia [54].

Zirconia or zircon is converted first to hydrous zirconia, then to zirconium oxychloride solution via reaction with hydrochloric acid. Sulphuric acid or ammonium sulphate is added to the zirconium oxychloride solution, followed by heating. Metallic impurities remain in the solution and need to be removed. However, some titanium remains because it is difficult to separate in this process. The sulphate is fired to zirconia [2, 12].

5.6.2 Oxychloride crystallisation

This method has been used, although it is considered to be too expensive because of the quantities of hydrochloric acid needed. It was used to produce zirconium oxychloride on a large scale. Traditionally, the product of chlorination of zircon or baddeleyite – zirconium tetrachloride contaminated with aluminium chloride, titanium tetrachloride, silicon tetrachloride and iron trichloride – is treated with 20% hydrochloric acid to produce zirconium oxychloride solution. The solution is gently heated to 65 °C. At this temperature, crystals start to form. The solution is allowed to stand for 24 hours and the temperature is kept above the crystallisation range by using hot water jackets [24, 54].

Crystals of zirconium oxychloride are dried at 85 °C and supplied for commercial use. To produce zirconia, zirconium oxychloride crystals are fired in air. A very hard and granular product is obtained. For fine zirconia, zirconium oxychloride is dissolved in water and ammonia is added to the precipitated zirconium hydroxide that is then fired to produce fine zirconia [54].

5.6.3 Precipitation with sulphur dioxide or sodium thiosulphate

This method is useful for producing zirconium compounds free from iron. Zirconium compounds hydrolyse much more readily than similar iron compounds. The precipitation of zirconium sulphate is hindered by the presence of sodium and potassium sulphates, but if these are present in only small amounts, the addition of sodium thiosulphate in excess will yield a good separation [54].

For successful precipitation with sodium thiosulphate, four conditions must be satisfied, namely:

- The solution must be only slightly acidic and relatively low in sodium and potassium.
- The solution should not be concentrated – a concentration of one part of zirconia to 50 parts of water is favourable.
- The addition of thiosulphate should be made to the solution heated to about 70 °C.
- After the addition of the thiosulphate solution, the solution should be allowed to stand for several hours to ensure complete precipitation.

For industrial use, it has been suggested that sulphur dioxide should be used to replace sodium thiosulphate, due to the large excess required, i.e. 500%. Sulphur dioxide is passed through a boiling solution of sodium zirconate diluted in hydrochloric acid. As a result, the zirconium precipitates completely [54].

5.6.4 Precipitation as phosphate

Zirconium phosphate is a useful compound for separating zirconium from other elements. It is insoluble in most strong mineral acids that retain most other elements in solution [54].

If hydrogen peroxide is added to the acid solution before the addition of phosphate ions, zirconium phosphate, unlike other phosphates, will still precipitate. The precipitate is, however, difficult to handle and the process will be difficult to operate on a large scale. There are some conditions to be followed [54]:

- The acidity of the hydrochloric or sulphuric acid solution of zirconium may vary from 3% to 20%.
- The solutions must be very dilute in relation to zirconium.
- The presence of hydrogen peroxide is essential to prevent the precipitation of titanium.
- The precipitation is hastened by heating or agitation.

Purity levels as high as 98% can be obtained. The process is referred to as being laborious and the result is not very satisfactory [54].

5.6.5 Purification as hydrated sulphate

The U.S. Bureau of Standards developed this method. The zirconium sulphate is claimed to be of a high purity, with a good yield [54]. In this process, zirconia or zircon is converted into a zirconate salt. The zirconate salt is hydrolysed and converted to sulphate or chloride zirconium solution. To that solution is added concentrated sulphuric acid. A crystalline white precipitate of zirconium sulphate, $Zr(SO_4)_2.4H_2O$, is formed. For purification, the crystals are dissolved in water, followed by reprecipitation of the hydrated sulphate. For the best results, one volume of sulphuric acid is added to two volumes of concentrated zirconium solution [2, 54].

5.6.6 Double fluorides procedure

Potassium zirconium fluoride may be prepared by dissolving zirconium oxide in hydrofluoric acid in lead vessels. Zirconium oxide that has been ignited at very high temperatures does not dissolve. After filtration, the solution is neutralised with a solution of pure potassium carbonate or hydroxide. Potassium zirconium fluoride precipitates as the solution cools down. The crystals are purified by recrystallisation [54].

It is difficult to separate impurities of titanium and iron by this method, and therefore repeated crystallisation to achieve a certain extent of separation is required and the starter zirconia material must be relatively pure. Titanium forms an analogous compound with the same solubility as the zirconium compound. Double fluoride prepared by this method had a purity of 99.99% [54].

5.6.7 Thermal decomposition of alkali chlorozirconates

Mixtures of zirconium tetrachloride and sodium chloride or potassium chloride are fused and decomposed by heating at 500 - 600 °C at atmospheric conditions. This has a double purpose. It physically traps the non-volatile matter and chemically binds those metal chloride impurities that can form alkali chloride double salts [54].

5.6.8 Sublimation of zirconium tetrafluoride

Zirconium tetrafluoride with high purity is prepared by the sublimation in vacuum of zirconium fluoride formed by the precipitation and dehydration method. The purification is achieved by sublimating zirconium tetrafluoride in hydrogen fluoride at 800 – 850 °C [12, 15, 54]. With high temperatures the impurities increase, but operating at lower temperatures slows the process of sublimation [54].

5.6.9 Mechanical processing

Using anhydrous zirconium tetrachloride as precursor, Dodd and McCormick [55] mixed it with lithium oxide and milled it for six hours in an inert atmosphere provided by an argon flux. After milling, the reactant mixture was heat-treated at 400 °C for 1 hour in the same inert atmosphere.

The lithium chloride by-product was removed by washing several times with deionised water and methanol in an ultrasonic bath. The powders were recovered by centrifugation. The powders were subsequently dried in air for several hours at 80 °C [55].

The proposed reaction for the process can be expressed in the following reaction scheme:

$$ZiCl_4 + 2Li_2O \rightarrow ZrO_2 + 4LiCl$$

Scheme 5.16: Reaction scheme of zirconium mechanical processing with lithium oxide [55]

Reaction between zirconium tetrachloride and lithium oxide occurs only after the low-temperature treatment. The reaction depends on the heating rate and also on the addition of lithium chloride as diluent. The addition of the diluent increases the size of the zirconia particles and thus reduces the average crystal size. This reduction is reported to favour the tetragonal phase [55].

Alternatively, magnesium oxide can be used and in this case the milling time is extended to 12 hours under the same conditions as for lithium oxide. The heat treatment must be conducted between 400 and 600 °C. The resulting reaction is shown in the following scheme [56]:

$$ZrCl_4 + 2MgO \rightarrow ZrO_2 + 2MgCl_2$$

Scheme 5.17: Reaction scheme of zirconium mechanical processing with magnesium oxide [56]

In the case of magnesium oxide, the reaction occurs during the milling process, unlike the reaction with oxides of calcium and lithium [56, 57], which needs supplementary heat for the reaction to take place. The reason for this difference is unknown [56].

The post-milling heat treatment is necessary to improve the crystallinity of the final zirconia powder. The zirconia produced is either tetragonal or cubic. The explanation for this is that the tetragonal phase has lower surface energy than the monoclinic phase, which is stable at ambient temperature. Thus a reduction in particle size to the nanometre regime can result in the stabilisation of high-temperature phases. However, it seems that this is not the real reason for the phenomenon [56].

5.6.10 Sodium metaphosphate method

This method is held to be appropriate for producing fully dense ceramics of uniform microstructure and thus consistent properties. These properties are desirable for mechanical and electrical applications [58].

In contrast to other process that involves solution precursors, this method avoids wet chemical processing. It produces tetragonal powders with approximately a particle size of 12 nm. This route is based on a solid-state reaction, at a relatively low temperature (500 °C), between sodium zirconate and sodium metaphosphate ($NaPO_3$). The reaction is represented by the following scheme:

$$Na_2ZrO_3 + NaPO_3 \rightarrow Na_3PO_4 + ZrO_2$$

Scheme 5.18: Reaction scheme of zirconia purification via the metaphosphate method [58]

The process produces sodium zirconate via the previously described processes of fusion. The reaction time ranges from 60 h to 100 h. For previous milled mixtures, 60 h is apparently sufficient [58].

5.7 Separation of Hafnium and Zirconium

Zirconium and hafnium are chemically and metallurgically very similar. They exhibit the same valences and have essentially the same ionic radii, 0.074 nm for Zr^{4+} and 0.075 for Hf^{4+}. For most uses, their separation is unnecessary. For nuclear power use, zirconium free of hafnium is necessary [12, 15].

The first method described by Coster and Hevesy uses fractional crystallisation of potassium or ammonium hexafluorozirconates [13]. Actually, four methods have been used industrially: fluoride salt crystallisation, methyl isobutyl ketone extraction, tributyl phosphate extraction and extractive distillation. Ion-exchange methods are also used for small-scale production [12, 13]. These methods are based on small differences in the equilibrium constants between zirconium and hafnium species. The use of differences in reaction rates has also been recommended [13].

5.7.1 Fluoride salt crystallisation

This consists of separating hafnium and zirconium by repeated crystallisation of hexafluorozirconate from hot aqueous solution. The solution is acidified to minimise oxide-fluoride salt formation. During each step the salt crystals are depleted of hafnium. This process has been used in the Ukraine [12].

5.7.2 Methyl isobutyl ketone extraction

This is based on the preferred extraction of hafnium dihydroxide thiocyanate from hydrochloric acid solution by methyl isobutyl ketone. This method was developed in the USA and is used by American producers [12, 15].

Zirconium-hafnium tetrachloride is dissolved in water to form dihydroxychlorides via hydrolysis in hydrochloric acid solution. The solution is mixed with methyl isobutyl ketone to extract iron as $HFeCl_4$ in the organic phase. Then ammonium thiocyanate is added to the dihydroxychloride solution. A mixture of dihydroxychloride and dihydroxythiocyanate of zirconium and hafnium is produced. The mixture is countercurrently mixed with methyl isobutyl ketone and thiocyanic acid solution to extract hafnium dihydroxide thiocyanate in the organic phase. Hafnium is recovered using dilute sulphuric acid in ketone solution [12, 15].

Zirconium is recovered from hydrochloric acid solution by heating the solution above 90 °C, adding precisely 2 mol of sulphuric acid for each 5 mol of zirconium and raising the pH carefully to 1.2 - 1.5 with dilute ammonium hydroxide. As a result, granular zirconium basic sulphate, $Zr_5O_8(SO_4)_2.xH_2O$, is precipitated. Zirconium basic sulphate is easily filtered and washed to remove aluminium and uranium impurities. The sulphate is mixed with ammonium hydroxide to convert it into hydrous zirconia, which is fired to produce pure zirconia [12, 15].

Organic reactants are recovered and reused. Considerable quantities of hydrochloric and sulphuric acid and ammonium are consumed. Zirconium produced via this process contains 35 - 90 ppm of hafnium. Hafnium contains 200 – 2 000 ppm of zirconium [12].

5.7.3 Tributyl phosphate extraction

This method was developed in France, Britain and the USA. It is used commercially in India to obtain zirconium for the nuclear industry. It has also been used commercially in the USA [12].

Hydrous zirconia and hafnia are dissolved in concentrated nitric acid. The solution is extracted countercurrently with tributyl phosphate solution in kerosene. Hafnium and most metallic impurities remain in the aqueous phase. Zirconium is recovered from the kerosene solution with dilute sulphuric acid solution, which causes it to precipitate, and it is then fired to pure zirconia [12].

5.7.4 Extractive distillation

Hafnium tetrachloride is slightly more volatile than zirconium tetrachloride. Thus, the two chlorides can be fractionally distilled if they are handled in the liquid state. This can be achieved by using a molten continuous solvent, $KCl\text{-}AlCl_3$, in which they are soluble. The distillation can therefore be conducted at atmospheric pressure [12, 15].

The mixture of zirconium-hafnium tetrachloride is heated above 437 °C, the triple point of zirconium tetrachloride. The hafnium tetrachloride and some zirconium tetrachloride are distilled. Pure zirconium tetrachloride remains [15].

5.8 Reduction to Metal

The first attempt to produce zirconium metal was made by Berzelius in 1824, using sodium-potassium hexafluorozirconate. The first pure zirconium was produced only in 1925, using the iodide thermal dissociation method [12, 15].

The reduction process is particularly difficult because of the strong tendency of zirconium to dissolve oxygen. Oxygen affects the properties of zirconium. Therefore, reducing agents must be oxygen-free, as well as nitrogen- and carbon-free [12, 15].

5.8.1 Kroll process

Zirconium metal is produced by reduction of zirconium tetrachloride with molten magnesium under inert conditions (argon or helium) [12].

Hafnium-free zirconia is mixed with pulverised coke and fed into an induction-heated chlorinator. The mixture is fluidised with chlorine gas. The reaction, at 900 °C, produces zirconium tetrachloride and carbon dioxide. Zirconium tetrachloride is collected in a nickel condenser below 200 °C, as a powder. Subliming and condensing again in a nitrogen-hydrogen atmosphere purifies the product. Such an atmosphere allows the reduction of the aluminium and phosphorus contents. The powder is placed in a cylindrical retort with magnesium casting ingots. The retort is repeatedly evacuated and filled with argon at 200 °C. Heat is then applied to the lower part of the retort to melt the magnesium ingots. Zirconium tetrachloride sublimes and is reduced to zirconium metal. Thereafter the retort is cooled down and unloaded. The bottom part of the reduced product contains "mud" – a thick suspension of tiny zirconium metal beads – under a layer of liquid magnesium chloride. Zirconium chloride is mechanically separated from the magnesium-zirconium metallic regulus [12, 15].

The regulus is then distilled to remove residual magnesium chloride and magnesium metal. At 980 °C magnesium chloride melts and is drained, while magnesium metal is condensed on the cold wall of the lower retort. Zirconium metal begins to sinter together. The porous mass obtained is known as zirconium sponge [12, 15].

5.8.2 Other reduction processes

Ductile zirconium has been commercially produced in a two-step sodium reduction of zirconium tetrachloride. In the first stage of the process, zirconium tetrachloride in vapour is continuously fed into a stirred argon-filled reactor containing sodium chloride. Zirconium tetrachloride is reduced to zirconium dichloride via the sodium. This step is very exothermic and the heat release rate determines the feed rate [12, 15].

The $ZrCl_2$-NaCl is transferred to a second reactor where the mixture is reheated with additional sodium. As a result, zirconium dichloride is reduced to zirconium metal. Sodium chloride is removed by leaching with water [12, 15].

The reduction can be achieved by using potassium hexafluorozirconate with calcium metal in a sealed bomb. This process is used in Russia. With calcium, zirconium tetrachloride can also be used [12, 15].

Zirconia can also be reduced with calcium or magnesium. Finely divided zirconium metal is recovered by leaching with cold hydrochloric acid. The powder is very pyrophoric due to the large surface area. The powder contains 0.3 - 0.5% of oxygen, so it cannot be malleable and ductile if melted in ingots [12, 15].

5.8.3 Electrolysis

This process has been considered as an alternative to the Kroll process, but it is difficult. Using only a chloride salts system is inefficient due to the lower stability of the chlorides in the melts. Adding a small amount of fluorine salts increases the stability of zirconium (IV) ions in solution, decreasing the concentration of the lower-valence zirconium ions. This raises the efficiency of the current [12, 15].

5.9 Refining

Kroll zirconium is pure and ductile for most applications. But for some other applications in which extremely soft metal is needed and, for research studies, further purification is required. Purification is achieved by the van Arkel-de Boer method, also called the "iodide-bar process". The van Arkel-de Boer process was the only one used from 1925 to 1945 to produce pure zirconium from zirconium ores. Nowadays, the method is only used only to produce zirconium of high purity [12, 15].

Iodide vapour is reacted with Kroll zirconium sponge or calcium-reduced metal powder to produce zirconium tetraiodide. Zirconium tetraiodide vapour diffuses to a heated filament, usually zirconium wire, where it is thermal dissociated, depositing zirconium and releasing iodine to be recycled [12, 15].

$$2I_2 + Zr \xrightarrow{250\text{-}300^\circ C} ZrI_4 \xrightarrow{1200\text{-}1500^\circ C} Zr + 2I_2$$

Scheme 5.19: Reaction scheme of zirconium refining process [12, 15]

The diameter of the filament grows as zirconium is deposited. Bars up to 40-50 mm in diameter can be grown from a zirconium filament 3 mm in diameter [12, 15].

Electron beam melting of zirconium has been used to remove more volatile impurities, such as iron and aluminium. This method is not usually used because the metal's vapour pressure at its melting point is higher than that of most impurities. The metal vapour pressure results in considerable losses in the high vacuum utilised in electron beam melting [12, 15].

6 ANALYTICAL METHODS

6.1. X-Ray Diffraction Spectroscopy

X-rays are defined as short-wavelength electromagnetic radiation produced by the deceleration of high-energy electrons or by electronic transitions involving electrons in the inner orbitals of atoms. The range of wavelengths is from 10^{-5} Å to about 100 Å. Conventional X-rays are confined to the region of approximately 0.1 Å to 25 Å [59]. The X-rays used in diffraction lie between 0.5 and 2.5 Å [59].

As with other types of electromagnetic radiation, the interaction of X-rays with particles in their pathway results in scattering. In a perfect crystal, scattering centres are located at fixed distances and spatially distributed in a regular way. Thus, at a certain angle of incident beam and a determined wavelength, the scattering will result in a constructive interference and maximum diffraction. The diffraction angles are intimately related to the interplanar distance of crystal sheets. This angle can be determined by *Bragg's Law* [59-61].

$$\sin\theta = \frac{n\lambda}{2d}$$

where θ is the angle of the incident beam on the crystal's surface; n is an integer; λ is the wavelength of the incoming X-ray radiation; and d is the interplanar distance of the crystal.

The interplanar distance of the crystal, d, in Bragg's equation is characteristic for each crystal structure. This is the basis of the X-ray powder diffraction method [59-61].

6.2 X-Ray Fluorescence Spectroscopy

A primary X-ray beam is focused on the sample in order to excite a secondary and characteristic X-ray beam. It is reasonable to think that the sample can be used as an X-ray source, thus producing the characteristic X-ray beam. This suggests the use of an electron beam as excitation source. The problem with such a procedure is that a conducting sample is needed and that most of the electron energy is converted into heat, causing problems of volatility [59-61].

The X-ray fluorescence method was used to quantify the different phases encountered during the different stages of the process. For quantitative purposes, it is sufficient to select one major line in the characteristic spectra of the element and relate that line to a concentration [59-61].

The X-ray spectrometer consists on an excitation source, a means of separating and isolating the characteristic lines, and a device for measuring characteristic line intensities [59-61].

7 EXPERIMENTAL

7.1 Introduction

This section describes the chemicals, apparatus and experimental procedure used.

7.2 Apparatus and Reagents

7.2.1 Reagents

Table 7.1: Reagents used

Name	**Purity**	**Supplier**	**Description**
Zircon	98.8%	Ferro Industrial Products	Powder
NaOH	Analytical grade	Bio-Zone Chemicals	Pellets
HCl	Analytical grade	Chemical Suppliers (Pty) Ltd	
H_2SO_4	Analytical grade	Bio-Zone Chemicals	
Methyl orange	Analytical grade	Riedel-de Haën	
Ammonium solution	Analytical grade	Chemical Suppliers (Pty) Ltd	

7.2.2 Apparatus

The following were used:

1. Moulinex coffee grinder.
2. Ohaus Explorer balance with a 2 100 g full-scale capacity and resolution of 0,01 g.
3. Fireclay crucibles resistant to alkalis.
4. Townson and Mercer low-temperature oven.
5. Model TPF 12/2 high-temperature oven.
6. Mortar and pestle.
7. Beckmann GPR model centrifuge with a maximum speed of around 5 000 r/min.
8. Mettler Delta model 340 pH meter.

7.3 Sample Preparation

Approximately 36.6 g of zircon from Ferro Industrial Products, with an average particle size of 9 µm, was weighed for each fusion experiment and ground in a Moulinex coffee grinder. To that a given amount of sodium hydroxide (e.g. 8, 16, 32 or 48 g) was added. The mixture was homogenised for approximately five minutes and then transferred to a previously weighed clay crucible.

The crucible with the mixture were weighed again and placed in the high-temperature oven, previously brought to the desired temperature. To prevent segregation of the sodium hydroxide, after 30 to 45 minutes the mixture was removed from the oven and ground using a mortar and pestle. After milling, the mixture was replaced in the oven.

After the required fusion time, the AFDZ (alkali fusion decomposed zircon) reaction mixture was allowed to cool at room temperature. The filled crucible was then weighed. The AFDZ was transferred to a beaker and the empty crucible was weighed to determine AFDZ losses.

7.3.1 Long fusion times

To identify the equilibrium phases, the fusion reaction must be allowed to take place over long periods of time. In the present case, the fusion reaction was run for 336 hours at four different mol ratios (1, 2, 4 and 6 mol of sodium hydroxide per mol of zircon) at 600, 650, 700, 750 and 850 °C.

A sample of the resultant AFDZ was analysed using XRD to identify the phases formed.

7.3.2 Leaching of the decomposed mixture

To the AFDZ in the beaker, 200 ml of distilled water was added and the mixture was stirred for 15 minutes. The supernatant liquid was decanted via centrifuging. The operation was repeated three times in order to maximise the removal of soluble salts and to hydrolyse the soluble silicates. To obtain optimum results, the mixture was gently heated while stirring.

7.3.3 Leaching solution

The leaching solution was collected in a beaker and titrated with standardised hydrochloric acid solution (32%). Methyl orange was used to identify the end-point of the titration. Alternatively, a pH meter was used to follow the titration, until pH ≈ 4.

To the titrated solution, an ammonia/ammonium chloride buffer solution was added to precipitate silica in hydrous form. This reaction is slow, so the mixture was left to rest for up to 12 hours to ensure complete precipitation.

The hydrous silica was separated by centrifugation at 5 000 r/min for 15 minutes. It was washed at least three times using 100 ml of distilled water. The water wash was decanted by centrifugation and purged.

The residual hydrous silica was dried in a low-temperature oven overnight, at 90 °C. The dried silica was transferred to a previously weighed alumina crucible, placed in a high-temperature oven at 900 °C and calcined overnight. The resulting calcined silica was weighed and expressed as a percentage of silica recovery.

7.3.4 Hydrolysis of zirconium salts

There are two zirconium salts that are formed as major components in this process: sodium zirconium silicate and sodium zirconate. Sodium zirconium silicate is insoluble in water, whereas sodium zirconate is soluble [12, 48]. When sodium zirconate is dissolved in water, it hydrolyses to hydrous zirconia. The excess of alkali produced by the hydrolysis reaction is eliminated by titration with standardised 32% hydrochloric acid solution.

To hydrolyse the sodium zirconium silicate, hydrochloric acid was added to the solution by titration. Standardised 32% hydrochloric acid solution was used, with methyl orange as indicator. This reaction is slow and therefore the titration was done slowly while stirring. A pH meter was used to follow the changes in pH until the desired pH of 3.8 was reached.

The residue of the supernatant liquid was separated by centrifugation for about 15 minutes and decantation. The residue was washed four to five times with distilled water, using centrifugation and decantation to eliminate the water.

7.3.5 Reaction with sulphuric acid

The residue containing mainly hydrous zirconia was reacted with sulphuric acid to produce acid zirconium sulphate tetrahydrate (AZST). A 5% stoichiometric excess of acid was used. The reaction was conducted at 150 °C with stirring. The excess sulphuric acid was removed by evaporation at 350 °C overnight in an oven.

The mixture of AZST and unreacted solids was separated by dissolution of zirconium sulphate in water. The heterogeneous mixture was separated by centrifugation and decantation. The liquid was crystallised at 90 °C and fired at 900 °C overnight to produce zirconia. The zirconia yield was expressed as mol percentage relative to the starting amount of zircon.

The remaining solids were dried at 90 °C and calcined overnight at 900 °C. The resulting residue was collected, weighed and expressed as a percentage of unreacted zircon.

7.3.6 Effect of fusion time on zirconia yield

The effect of fusion time on conversion was studied at 750 and 850 °C. Fusions were conducted with 2 and 4 mol of sodium hydroxide per mol of zircon for 1, 2, 4, 24 and 336 hours.

7.3.7 Effect of fusion temperature on zirconia yield

The effect of fusion temperature on the equilibrium product spectrum was evaluated from the 336-hour fusion data. Five fusion temperatures were chosen, namely 600, 650, 700, 750 and 850 °C. During these fusions, the samples were intermittently milled using a mortar and pestle to homogenise the reaction mixture.

7.4 Direct Synthesis of Zirconia from Zircon

It has been reported that sodium zirconate hydrolyses completely [2,12,15] to hydrous zirconia in water. Hydrous zirconia can be fired directly to zirconia. A brief literature review showed that there have been no attempts to optimise this potential route of zirconia production. An attempt was therefore made to produce zirconia directly using this route, as described below.

7.5 Experimental Procedure

Sample preparation was done as before. Fusions were conducted with 4 and 6 mol of sodium hydroxide. The water-leaching procedure was as described above. The residue was titrated and washed as before. The remaining residue was calcined and the product was expressed as zirconia yield.

7.5.1 Purity test

To test the purity of the zirconia produced in this way, a sample of leached and titrated decomposed zircon was divided into two portions. One was calcined directly, following the previously described procedure. The final product was weighed as zirconia. Sulphuric acid was added to the product, following the procedure described in Section 7.3.5.

The second portion was treated directly with sulphuric acid, as described in Section 7.3.5, and fired to zirconia. The results were then compared.

7.5.2 Work solutions

Standardisation of hydrochloric acid solution

To standardise the hydrochloric acid solution used in titrations, a certain quantity of sodium hydroxide was accurately weighed (approximately 2 g) to a beaker and dissolved in water. This solution was titrated with hydrochloric acid, using methyl orange as indicator.

Methyl orange solution

A 0.01% methyl orange indicator was used, prepared by direct dissolution of methyl orange powder in distilled water. This solution changes colour from red to yellow in the pH interval from 3.2 to 4.4.

7.6 Analysis

7.6.1 X-ray powder diffraction (XRD)

For phase identification, X-ray diffraction was performed with a Siemens D-501 automated instrument. The working line was Cu-Kα (1.542 Å). Measurements were taken between 0.8 and 10°. The receiving slit was placed at 0.04°. The counting area was from 4° to 70° on a 2θ-scale. The step time (counting time) was 15 seconds.

7.6.2 X-ray fluorescence (XRF)

Elemental analysis was done in an ARL9400+ wavelength-dispersive instrument. The samples were ground to a particle size of less than 75 μm in a tungsten carbide milling vessel. The ground samples were then roasted at 1 000 °C to determine the loss on ignition (LOI) value. To 1 g of the sample, 9 g of lithium tetraborate was added and the mixture was fused into a glass bead. All the possible elements present in the sample were then analysed.

7.6.3 Scanning electron microscopy (SEM)

The particle morphology was examined by scanning electron microscope using a JEOL JSM-840 instrument. The current was 3×10^{-11} amperes and the acceleration voltage was kept constant at 5.0 kV.

Process step	**Notes**
$ZrO_2.SiO_2$ + x NaOH	
1 $\downarrow$ 650 °C – 850 °C	1. Fusion (Choose reaction conditions to maximise yield of sodium silicates and avoid formation of sodium zirconium silicates.)
Na_2ZrO_3 + Na_2SiO_3 + Na_2ZrSiO_5	
2 $\downarrow$ water leach	2. Cool down and mill. Remove sodium silicates and unreacted NaOH using a water leach.
$Zr(OH)_4.xH_2O$ + Na_2ZrSiO_5	
3 $\downarrow$ HCl to pH = 3.8	3. Neutralise to hydrolyse sodium salts.
4 $\downarrow$ leach	4. Remove remnant sodium as NaCl using a water leach.
$Zr(OH)_4.xH_2O$	
5 $\downarrow$ H_2SO_4 (stoichiometric)	5. *In situ* formation of basic sulphate at 120 °C. It is insoluble in water and very stable towards dilute HCl.
$Zr_5O_7(SO_3)_3.nH_2O$ + SiO_2 + $ZrSiO_4$	
6 $\downarrow$ dilute HCl wash	6. Purification: Remove impurities including iron and radioactive elements.
$Zr_5O_7(SO_3)_3.nH_2O$ + solid residue	
7 $\downarrow$ H_2SO_4 (excess)	7. AZST formation. The acid sulphate is soluble in water.
8 $\downarrow$ roast @ 350°C	8. Evaporate excess sulphuric acid.
9 $\downarrow$ add water	9. Dissolve acid sulphate.
10 $\downarrow$ filtration	10. Remove silica from AZST solution.
$Zr(SO_4)_{2\,(aq)}$	
11 $\downarrow$ crystallisation, 90 °C	11. Crystallisation.
$Zr(SO_4)_2.4H_2O$ [high purity]	
12 $\downarrow$ calcination, 900 °C	12. Calcination.
ZrO_2 [high purity]	

Scheme 7.1: Outline of the De Wet alkali fusion process for acid zirconium sulphate

8 RESULTS

The main focus of this study was on optimising the fusion step in the De Wet process for the beneficiation of zircon sand. In this chapter, the yield and XRD results obtained for the alkali-decomposed zircon are reported. All the detailed XRD spectra are contained in Appendix A.

The composition of the zircon raw material from Ferro Industrial Products was determined using X-ray fluorescence (XRF). Table 8.1 shows the results. The raw material contained in excess of 98% zircon. Appendix A shows the XRD spectrum for the zircon raw material used in this study, as well as a spectrum for pure zirconia from Aldrich Chemicals with a purity of 99% and a particle size of 9 µm. The latter is the main end product sought in this investigation. The zircon XRD pattern shows an intense peak at 27° on the 2θ scale. Other peaks are located at 20°, 35.7° and 53.5°, with media intensity. In the zirconia XRD spectrum, the intense peaks are located at 28.2° and 31.6°. There is a series of medium intensity peaks.

Table 8.1: Composition of zircon raw material

Component		ZrO_2+HfO_2	SiO_2	Ti	Fe	Ca	P	U	Th
Concentration	ppm	65.7%	33.6%	738	683	666	455	331	144

ppm: parts per million on a mass basis.

8.1 Long Fusion Times

In order to establish the equilibrium products for the zircon and sodium hydroxide reaction, 336-hour experiments were conducted. These reactions were conducted at different temperatures and different reactant ratios, with intermediate milling every 24 hours. Appendix A shows the XRD spectra of the alkali fused decomposed zircon (AFDZ). Table 8.2 shows the main phases identified from the XRD spectra at the given fusion temperatures and mol ratios. Kwela [16] has reported additional data, especially at 650 °C.

Table 8.2: Equilibrium phases identified in the XRD spectra of AFDZ produced after fusion at 336 hours, with intermediate milling after every 24 hours, at different temperatures

NaOH:ZrSiO$_4$	**Temperature (°C)**	**Phases**			
		ZrSiO$_4$	**Na$_2$ZrO$_3$**	**Na$_2$ZrSiO$_5$**	**Na$_2$SiO$_3$**
2:1	600	Major	Minor	-	Minor
2:1	650	Major	Major	-	Minor
2:1	700	Major	Major	Major	Minor
1:1	750	Major	Minor	Major	-
2:1	750	Major	Major	Major	Minor
4:1	750	-	Major	Trace	Minor
2:1	850	Trace	Trace	Major	-
4:1	850	-	Major	Major	-
6:1	850	-	Major	-	Minor

8.2 Effect of Fusion Time

To study the effect of fusion time on conversion, experiments were conducted over 1, 2, 4, 24 and 336 hours, at a fusion temperature of 850 °C. Table 8.3 summarises the phase data obtained from the XRD spectra listed in Appendix A.

Table 8.3: Phases identified in the XRD spectra of AFDZ produced by fusion at 850 °C using different fusion times and mol ratios

NaOH:ZrSiO$_4$	**Time (hours)**	**Phases**			
		ZrSiO$_4$	**Na$_2$ZrO$_3$**	**Na$_2$ZrSiO$_5$**	**Na$_2$SiO$_3$**
1:1	48	Major	-	Minor	-
2:1	1	Major	Minor	Trace	Minor
2:1	2	Major	-	Major	Minor
2:1	4	Major	Minor	Major	Minor
2:1	24	Major	-	Major	Minor
2:1	48	Major	-	Major	-
4:1	2	Minor	Major	-	-

8.3 Effect of Stoichiometry on Two-hour Fusions

Appendix A also shows the XRD spectra for the other experiments conducted at various temperatures, times and mol ratios. Table 8.4 lists the phases identified in the XRD spectra of AFDZ obtained by fusion at 850 °C.

Table 8.4: Phases identified in the XRD spectra of AFDZ produced by fusion at 850 °C for 2 hours and different mol ratios

NaOH:$ZrSiO_4$	**Phases**			
(mol)	**$ZrSiO_4$**	**Na_2ZrO_3**	**Na_2ZrSiO_5**	**Na_2SiO_3**
2:1	Major	Major	Major	Minor
4:1	Minor	Major	Trace	Trace

8.4 Fusion Times at Other Temperatures

In order to understand the kinetics of reaction of the alkali fusion process, fusions were also conducted at other temperatures, i.e. at 650 and 750 °C. Table 8.5 shows the phases identified in the fused reaction products from the XRD spectra listed in Appendix A.

Table 8.5: Observed phases in the XRD spectra of samples fused at 650 and 750 °C

NaOH:$ZrSiO_4$	**Time**	**Temperature**	**Phases**				
(mol)	**(h)**	**(°C)**	**$ZrSiO_4$**	**Na_2ZrO_3**	**Na_2SiO_3**	**$Na_6Si_2O_7$**	**Na_4SiO_4**
2:1	2	650	Major	Minor	Trace	-	-
2:1	4	650	Major	Minor	-	-	-
4:1	1	650	Major	Major	-	Minor	-
4:1*	2	650	Major	Major	-	Minor	-
4:1	4	650	Major	Major	-	-	Minor
4:1*	24	650	Major	Major	-	-	-
6:1	1	650	Minor	Major	-	-	Minor
6:1*	2	650	Trace	Major	-	Minor	Minor
4:1*	4	700	Major	Major	-	-	-
2:1	2	750	Major	-	Minor	-	-
4:1	2	750	Major	Major	-	-	Minor

*Sample poorly crystallised.

8.5 Direct Synthesis of Zirconia

The direct synthesis of zirconia requires the exclusive formation of sodium zirconate. Experiments were therefore conducted to maximise this phase in the fusion products. Fusions were conducted at 650 and 750 °C, using 2 to 6 mol of sodium hydroxide per mol of zircon. Fusion times were varied from 2 to 48 hours. Table 8.5 also reports on the phases identified in the XRD spectra of these decomposition products.

9 DISCUSSION

9.1 Long Fusion Times: Equilibrium Phases

Long fusion times were investigated to determine which equilibrium phases would form as a function of temperature and composition. Fusion experiments were conducted for 336 hours, at different temperatures and various NaOH:$ZrSiO_4$ mol ratios. The conclusions drawn below are based on the interpretations of the XRD spectra listed in Appendix A and tabulated in Table 8.2.

When 1 mol of zircon is fused with 2 mol of sodium hydroxide, zircon and Na_2ZrO_3 are the main reaction products at 600 °C and 650°C. The XRD spectra also reveal the presence of minor amounts of crystalline sodium metasilicate. The observed product spectrum for these temperatures is consistent with the reaction shown in Scheme 9.1 below.

$$ZrSiO_4 + 4NaOH \rightarrow Na_2ZrO_3 + Na_2SiO_3$$

Scheme 9.1: Reaction observed at 600 and 650°C when 2 mol of sodium hydroxide were fused with 1 mol of zircon for 336 hours

The XRD peaks for Na_2ZrO_3 are more intense for the 650°C fusion than the 600°C reaction. This implies improved conversion of zircon to sodium metazirconate at the higher reaction temperature. At a fusion temperature of 700 °C, Na_2ZrSiO_5 appears as a new phase in the XRD spectrum. This suggests the occurrence of an additional reaction, as shown in Scheme 9.2.

$$ZrSiO_4 + 2NaOH \rightarrow Na_2ZrSiO_5$$

Scheme 9.2: Reaction observed above 700 °C when 2 mol of sodium hydroxide were fused with 1 mol of zircon for 336 hours

Above 750 °C, $ZrSiO_4$, Na_2ZrO_3 and Na_2ZrSiO_5 are the major equilibrium phases. Although sodium zircon ate appears as a major phase at 750 °C and a 2:1 stoichiometry, its peak intensities are clearly reduced compared with those at the 700°C fusion temperature. This indicates that the formation of sodium zirconium silicate is favoured over sodium zirconate at low mol ratios and high temperatures.

At 850 °C, the XRD spectrum of the AFDZ produced by fusion of 2 mol of sodium hydroxide with 1 mol of zircon for 336 hours shows that Na_2ZrSiO_5 is virtually the sole equilibrium phase formed. Only traces of Na_2ZrO_3 and zircon remain.

As expected, increasing the ratio of sodium hydroxide to zircon increases the sodium zirconate yield. The apparent presence of ZrO_2 (as reported on Spectrum 10 in Appendix A) may be an artefact of sodium carbonate as the XRD peaks of these two compounds show considerable overlap (see Spectrum 12 in Appendix A). The phases observed at 850 °C using the 4:1 stoichiometry indicate that the products may be explained by reactions 9.1 and 9.2 occurring simultaneously. The overall reaction is shown in Scheme 9.3.

$$ZrSiO_4 + 4NaOH \rightarrow xNa_2ZrO_3 + (2x\text{-}1)Na_2SiO_3 + (1\text{-}x)Na_2ZrSiO_5 + (1\text{-}x)Na_4SiO_4$$

Scheme 9.3: Reaction observed at 850 °C when 4 mol of sodium hydroxide were fused with 1 mol of zircon for 336 hours

The formation of sodium orthosilicate (Na_4SiO_4) can be explained by the reaction shown in Scheme 9.4.

$$ZrSiO_4 + 6NaOH \rightarrow Na_2ZrO_3 + Na_4SiO_4$$

Scheme 9.4: Reaction explaining the formation of sodium orthosilicate

A key observation is that sodium zirconium silicate does not form when fusing below 700 °C. This implies that sodium zirconate is the equilibrium phase at low temperatures.

9.1.1 Phase diagrams

Figures 9.1 and 9.2 show simplified phase diagrams previously reported by Manhique *et al.* [3]. They were constructed from the phases observed in the XRD spectra for 336-hour fusions. The vertical dotted line in these figures shows the locus of increasing the reactant ratio of NaOH to zircon used in the current experiments. Note that the phase $Na_4Zr_2Si_3O_{12}$, reported by D'Ans *et al.* [62] was not observed in this study. However, it was observed by Kwela [16] when fusing 4 mol of NaOH with 3 mol of zircon at 850 °C.

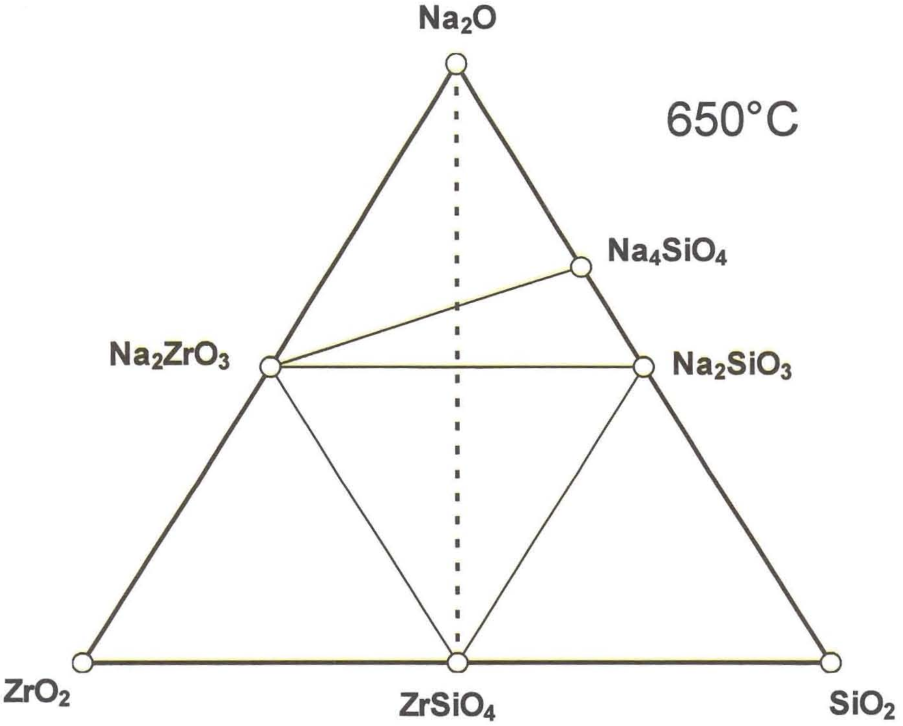

Figure 9.1: Simplified phase diagram for alkali decomposition of zircon at 650 °C

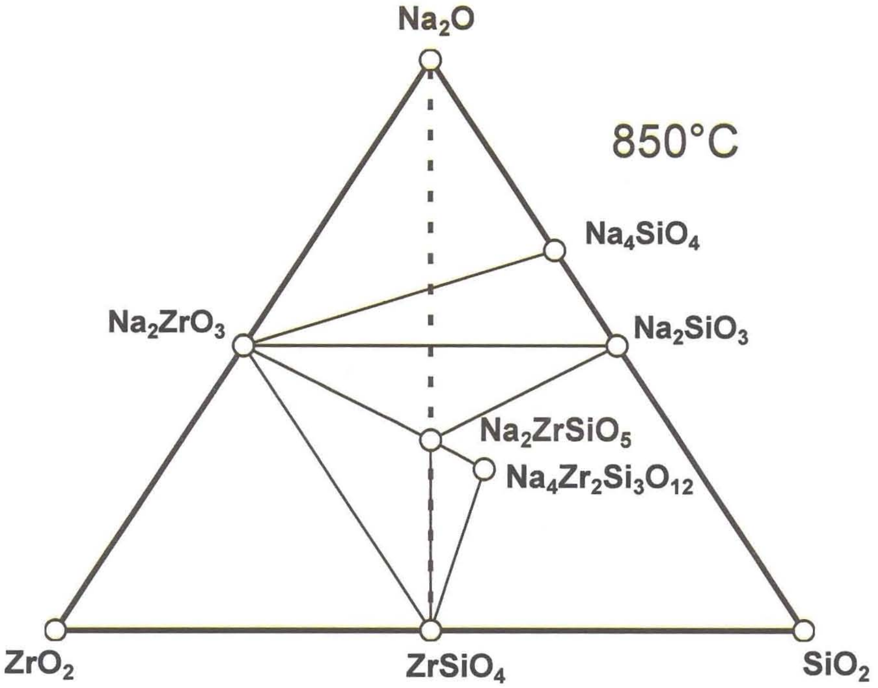

Figure 9.2: Simplified phase diagram for alkali decomposition of zircon at 850 °C

Figure 9.1 applies for fusions conducted at 650 °C, as well as at 600 °C. Figure 9.2 indicates the equilibrium product spectrum for reactions conducted at higher temperatures. The latter is similar to the phase diagram accepted in the literature for fusing zircon with sodium carbonate at temperatures above 1 000 °C [62].

9.1.2 Effect of fusion time on zirconia yield

The effect of fusion time on zirconia yield was studied. Fusions were conducted over fusion times of 1, 2, 4, 24 and 336 hours, using 2 and 4 mol of sodium hydroxide per mol of zircon in the fusion. The results are shown graphically in Figures 9.3 and 9.4.

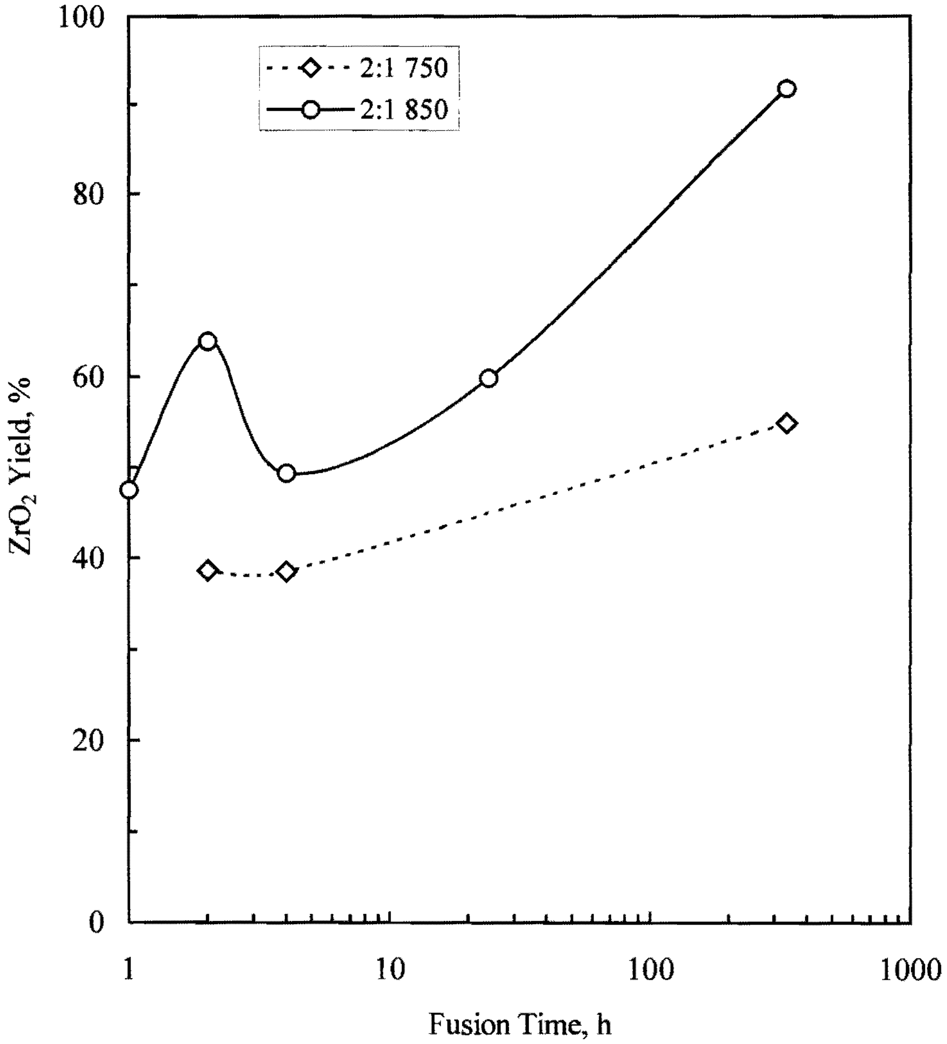

Figure 9.3: Effect of time on zirconia recovery at 750 and 850 °C, using 2 mol of sodium hydroxide per mol of zircon. A local maximum in the yield is observed at 2 hours of fusion

The zirconia yield curve at 850 °C shows an unexpected local maximum (of about 63%) at the 2-hour fusion point. Silica recovery also shows a local minimum of about 22% here. A minimum (≈ 49%) in the zirconia yield is observed at 4 hours of fusion. This roughly corresponds to the maximum in the silica recovery. Similar behaviour is observed at 750 °C (Figures 9.4 and 9.5).

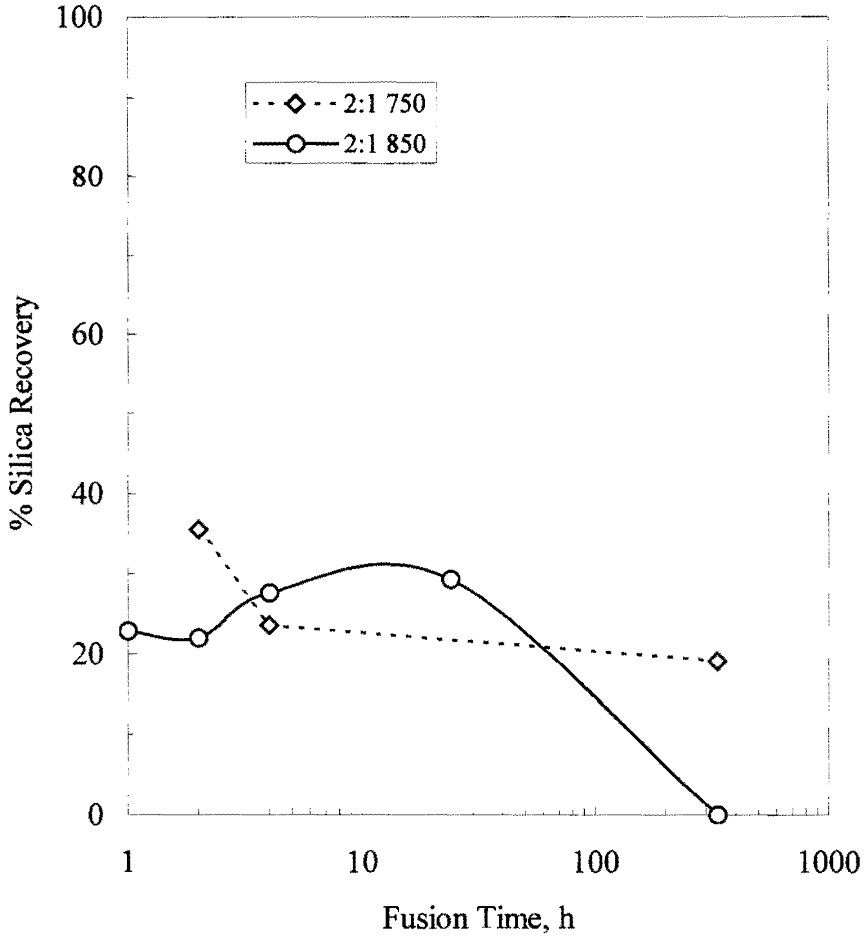

Figure 9.4: Silica recovery at 750 and 850 °C using 2 mol of sodium hydroxide per mol of zircon sand

Silica recovery reaches a minimum at 850 °C for 336 hours for the 2 mol stoichiometric ratio. This is consistent with the formation of Na_2ZrSiO_5, which is stable with respect to water, i.e. the compound does not hydrolyse in pure water. Consequently, sodium cannot be leached with water washing. The XRD results confirmed the formation of this phase (see Spectrum 9 in Appendix A). For the fusion at 750 °C, the silica recovery at 336 hours is still as high as 19% (Figure 9.4). This suggests the presence of soluble sodium silicates in the product spectrum and therefore, by implication, also Na_2ZrO_3. This is confirmed by Spectrum 7 in Appendix A. Note that the sodium silicates do not crystallise easily and it is easier to infer their presence by indirect means in the XRD.

For 4 mol, similar behaviour is observed, i.e. at 2 hours and 850 °C there is a local maximum in the zirconia yield of ca. 76% (Figure 9.5). Figure 9.6 shows the silica recovery using 4 mol of sodium hydroxide per mol of zircon.

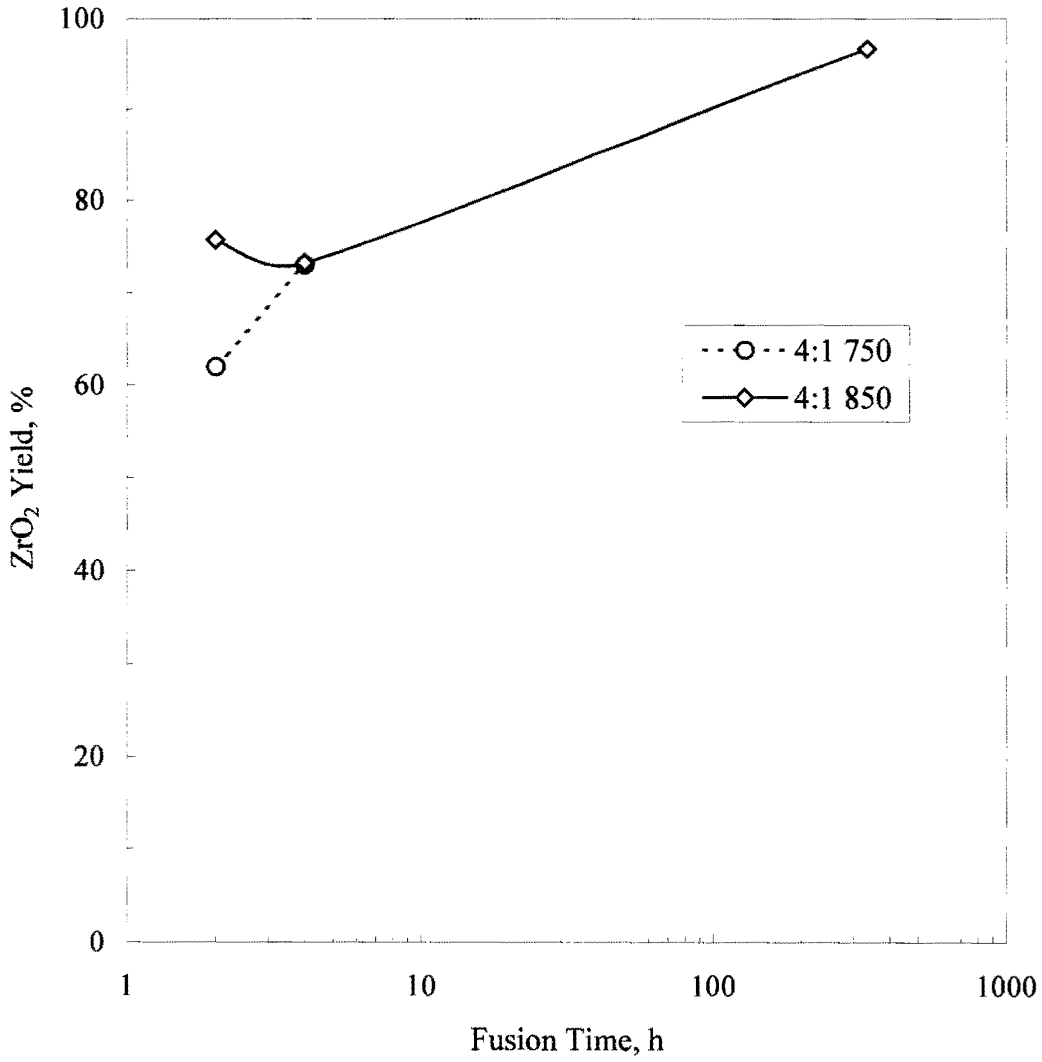

Figure 9.5: Effect of time on zirconia recovery at 750 and 850 °C using 4 mol of sodium hydroxide per mol of zircon sand

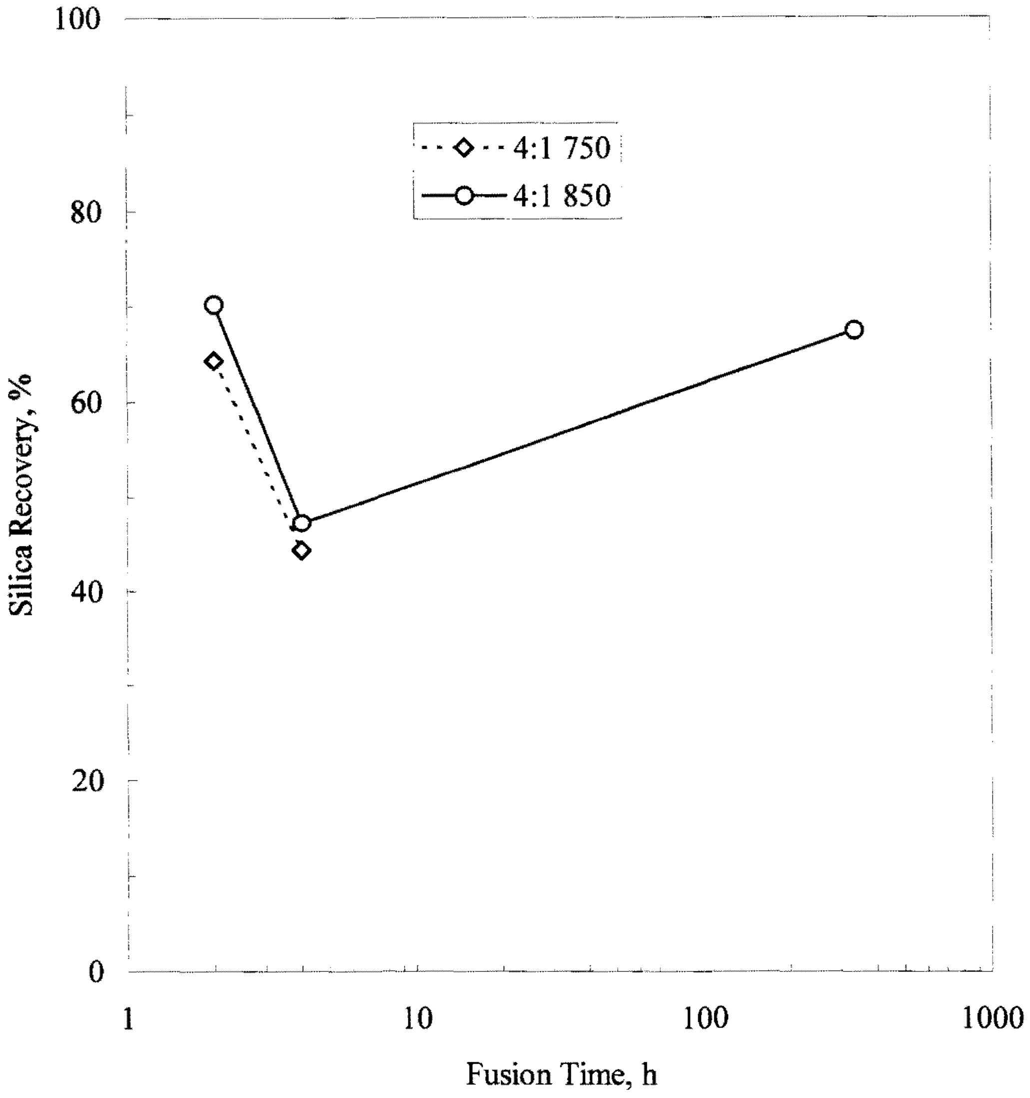

Figure 9.6: Silica recovery at 750 and 850 °C using 4 mol of sodium hydroxide per mol of zircon sand

9.2 Optimisation of Zirconia Yield at Two Hours Fusion Time

Commercially, short fusion times would be preferred. Based on this fact and the yield maximum observed with the 2-hour fusions, further experiments were limited to this fusion time. The effects of fusion temperature and stoichiometry on zirconia yield were studied and the results are presented in Figure 9.7. The zirconia yield shows a monotonic increase with temperature and mol ratio.

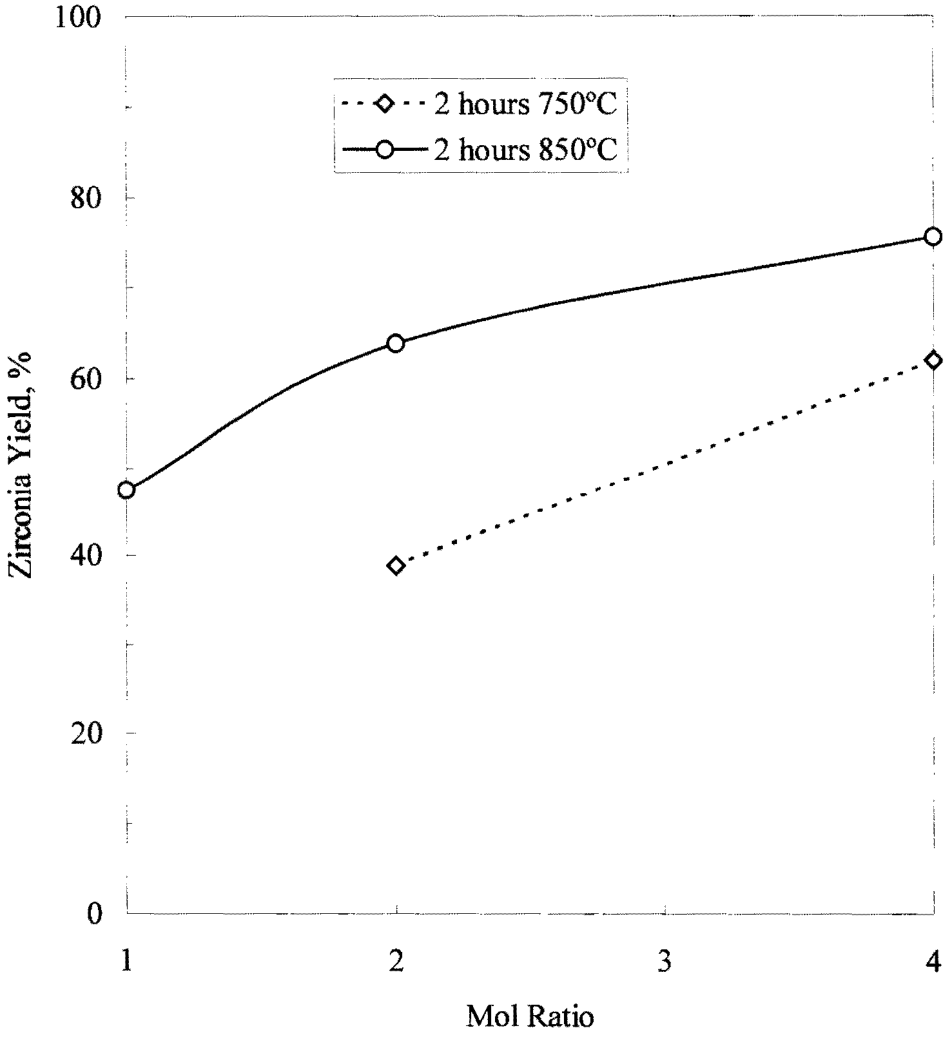

Figure 9.7: Effect of the stoichiometry of the reaction on zirconia yield after 2 hours of fusion

Silica recovery shows a minimum when 2 mol of sodium hydroxide are used at 850 °C for 2 hours. This is attributed to the formation of Na_2ZrSiO_5 (see Spectrum 8 in Appendix A).

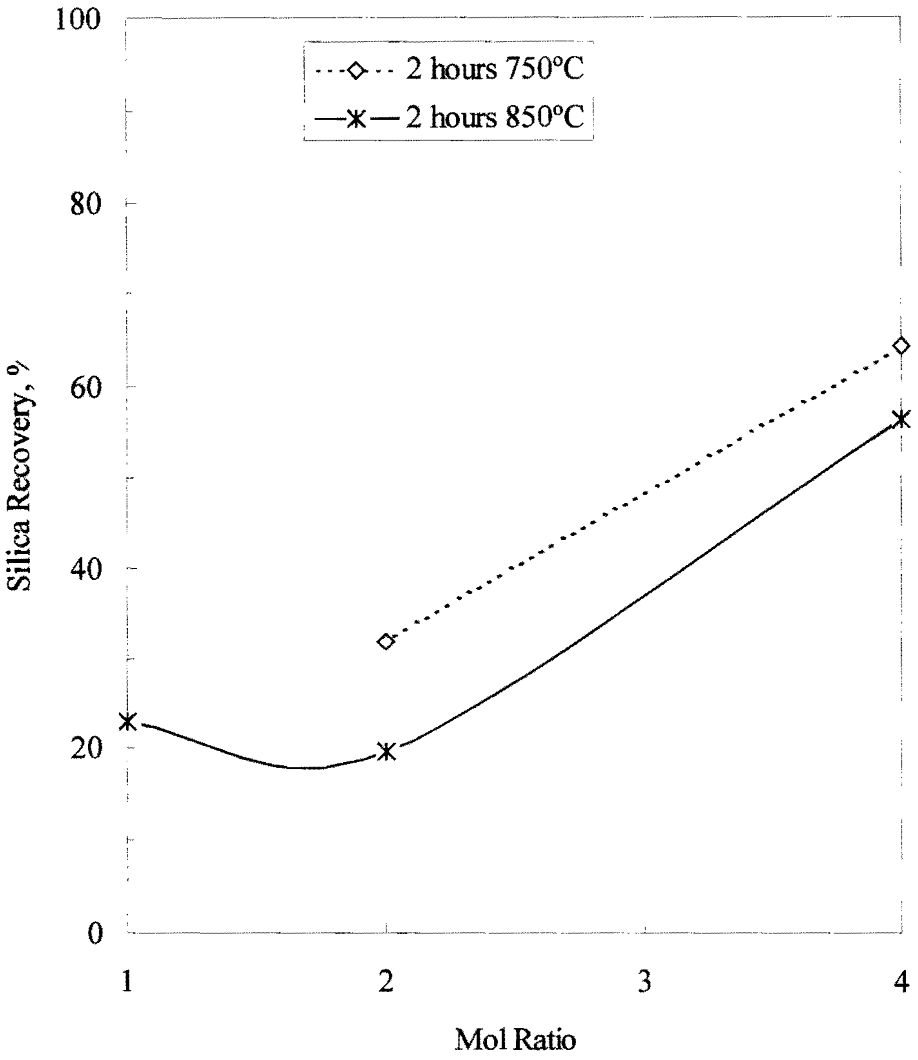

Figure 9.8: The effect of stoichiometry on silica recovery at 750 and 850 °C fusion temperatures

9.3 Efficiency of the Process

The efficiency of the process was tested by studying the zirconia yield relative to the amount of sodium hydroxide consumed (mass per mass basis), at 650, 750 and 850 °C, using 2, 4 and 6 mol at 2 hours fusion time. The results are presented in Figure 9.9. The highest reagent efficiency is attained for fusions conducted at 850 °C using 2 mol of sodium hydroxide.

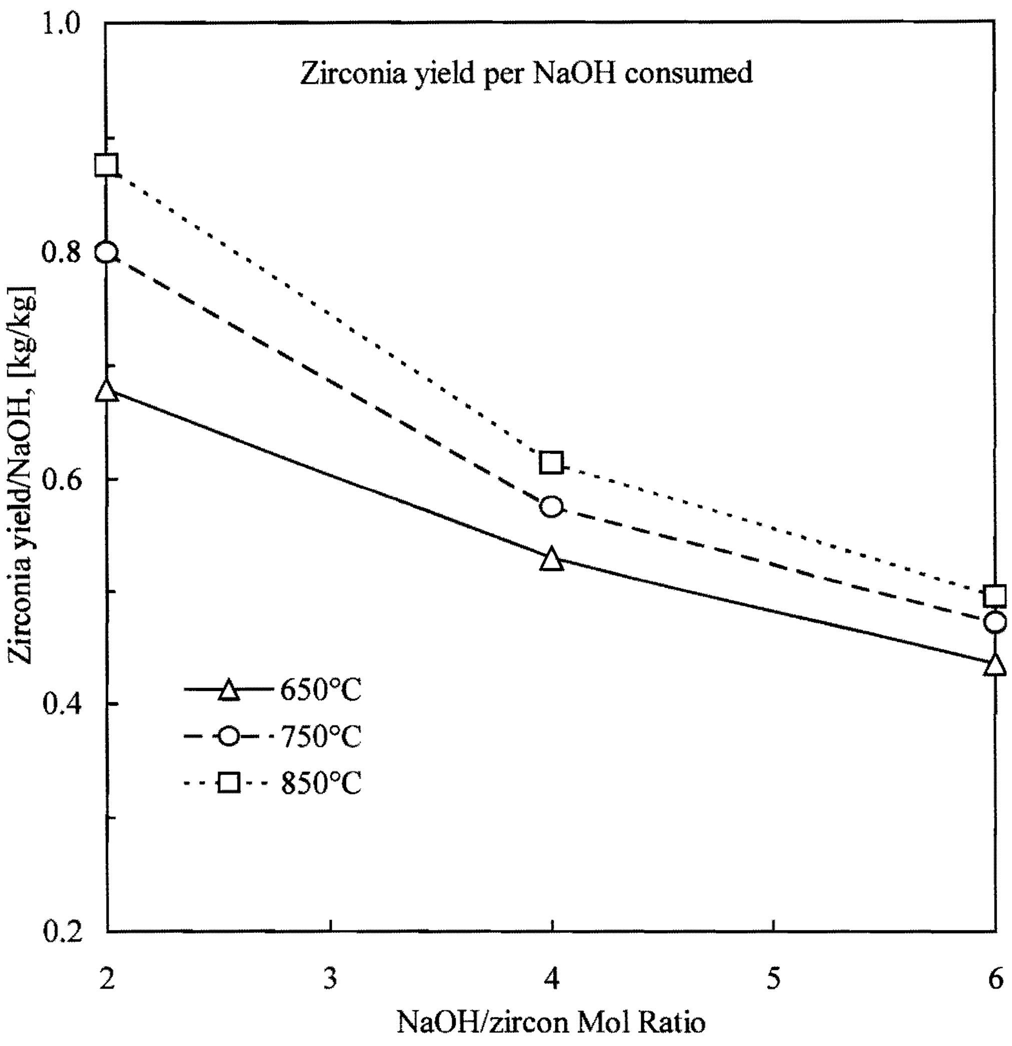

Figure 9.9: Efficiency of the process analysed for the effects of fusion temperature, stoichiometry for 2-hour fusion times

The process also allows the recovery of alkali in the form of a saleable sodium silicate product stream. The formation of Na_2ZrSiO_5 exacerbates the generation of waste, as it has to be hydrolysed using acid. This not only creates a salt-based waste stream, but also consumes additional acid reagent. Figure 9.10 shows that fusions conducted at 850 °C using 2 mol of sodium hydroxide also yield the lowest amount of salt waste.

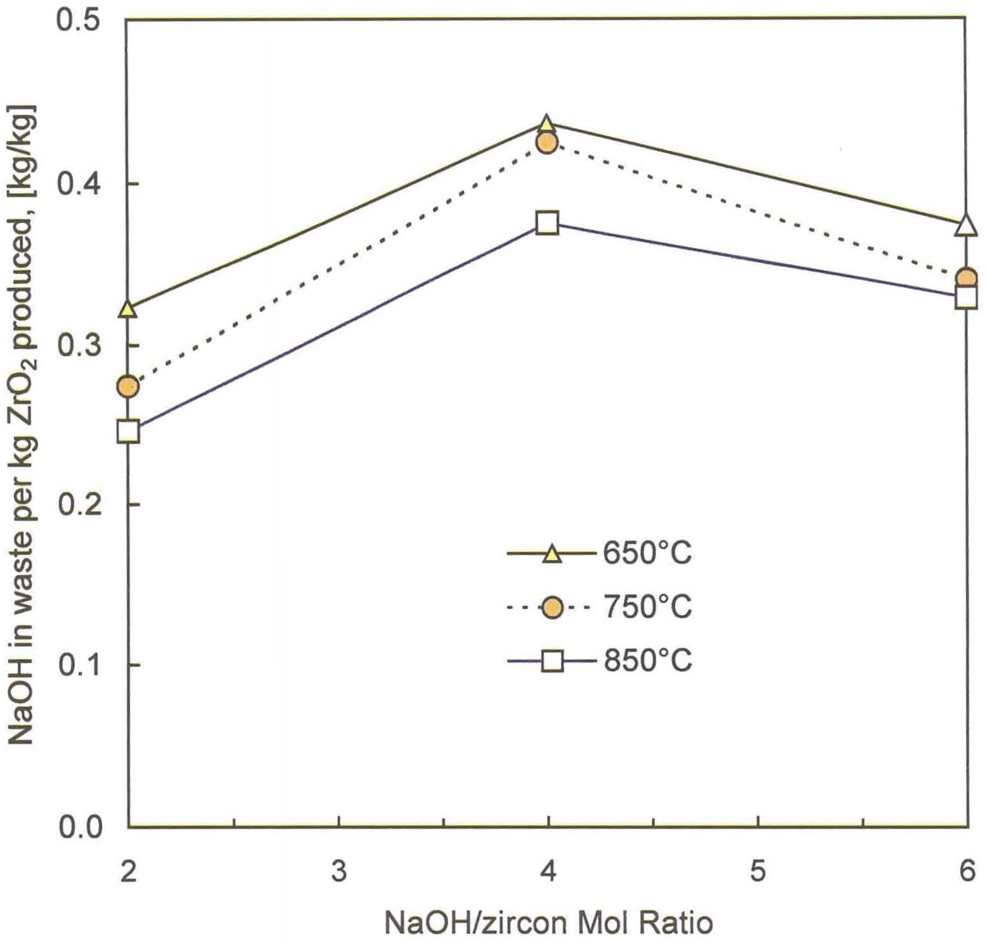

Figure 9.10: Generation of salt waste stream by the process, analysed for the effects of fusion temperature, stoichiometry for 2-hour fusion times

9.4 Possible Explanation for Na_2ZrO_3 Formation to the Detriment of Na_2ZrSiO_5 Formation

The 336-hour fusions at high temperatures showed that Na_2ZrSiO_5 is the equilibrium phase at a mol ratio of 2:1. The formation of this phase also guarantees the most efficient use of alkali for the liberation of zirconia from zircon. Thus the local yield maxima observed at a 2-hour fusion time in Figures 9.3 and 9.5 are due to the initial formation of this phase. However, as the fusion time is extended, the proportion of this phase in the product tends to decline before increasing again. This presents a paradox: How does one explain the temporary disappearance of the equilibrium phase once it has been formed? An attempt is made below to provide a rationalisation of these observations.

Zircon is a highly refractory compound with a melting point above 2 550 °C. The sodium hydroxide reagent melts at about 318 °C. Thus it is reasonable to assume that a "shrinking core" model applies to the decomposition reaction. During the fusion reaction, the liquid-like high-basicity outer layer etches away the surface of the solid zircon particle. In the process, the composition of the liquid phase changes. A progressive change in basicity is expected as the reaction proceeds to completion. With regard to the phases observed in the XRD, the progress of the reaction under ideal conditions and for 1 mol of zircon reacting with 2 mol of NaOH can be described in terms of the following product spectrum:

Initially: $ZrSiO_4 + 2NaOH$
Intermediate: $x Na_2ZrO_3 + y Na_2SiO_3 + z Na_4SiO_4 + u Na_2ZrSiO_5 + v ZrSiO_4 + w NaOH$
Complete conversion: Na_2ZrSiO_5

This scheme is connected to the experimental results obtained via the following additional assumptions:

1. The reaction does not proceed to completion.
2. The zirconia yield reflects the formation of Na_2ZrO_3 and Na_2ZrSiO_5.
3. The solid residue consists of unreacted zircon and silica only. Thus the zirconium remaining in the residue can be calculated from the zirconia yield.
4. From this, the silica content of the residue can be determined.
5. All the silica in the sodium silicate stream stems from the soluble Na_2SiO_3 and Na_4SiO_4, accepting that the $Na_4Si_2O_7$ is a linear blend of the previous two species.
6. The total amount of silica, i.e. the silica in the sodium solution plus the silica in the residue, is equal to the amount of zirconia, on a mol basis.

From these assumptions, we can establish the following mass balance equations:

Zirconia yield: $Zr_Y = x + u$
Zircon in the residue: $v = 1 - x - u$
Silica in the residue: $\mathrm{Si_R} = \mathrm{u}$
Silica in the sodium silicate stream: $Si_{SS} = y + z$
Total mol of silicon equals mol of zirconium: $y + z + u + v = x + u + v$
Therefore: $y + z = x$

From these relationships, it can be deduced that:

- the mol of Na_2ZrSiO_5 present (u) equals the mol of silica in the residue; and
- The quantity of Na_2ZrO_3 present equals the zirconia recovered minus the silica in the residue.

Since all these quantities were measured, the change in the product spectrum can be determined. The results are shown in Figure 9.11.

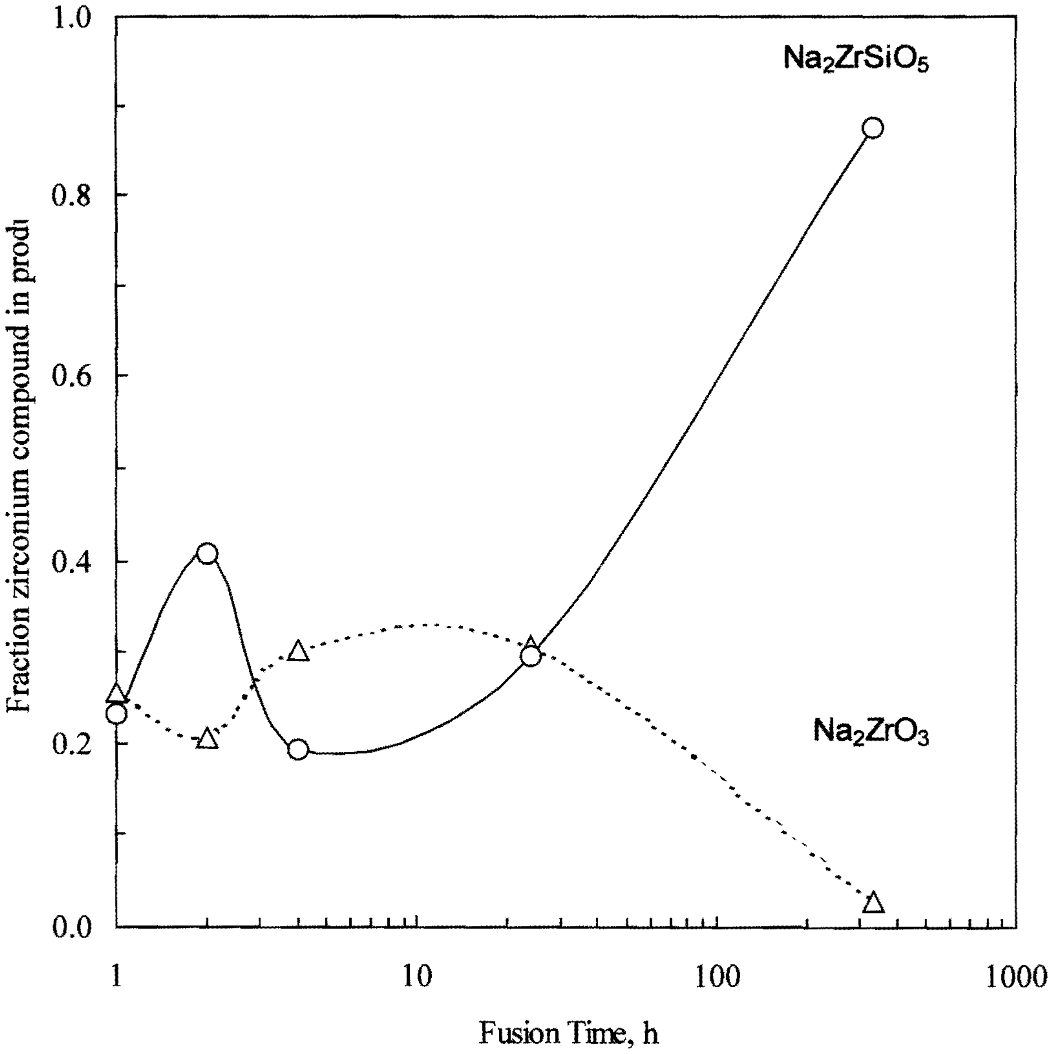

Figure 9.11: Correlation of fractions of Na_2ZrO_3 and Na_2ZrSiO_5, from mass balance

From the graph it can be seen that initially the phases Na_2ZrO_3 and Na_2ZrSiO_5 were formed in the same proportion, at the 1-hour fusion point. At 2 hours, the concentration of Na_2ZrSiO_5 is higher but it then falls to a minimum at about 4 hours, after which its concentration again increases. This observed behaviour confirms the paradox: it is observed that the final equilibrium product initially forms, then wanes and then reforms. The explanation might be that the actual products in equilibrium with the melt depend on the composition of the latter.

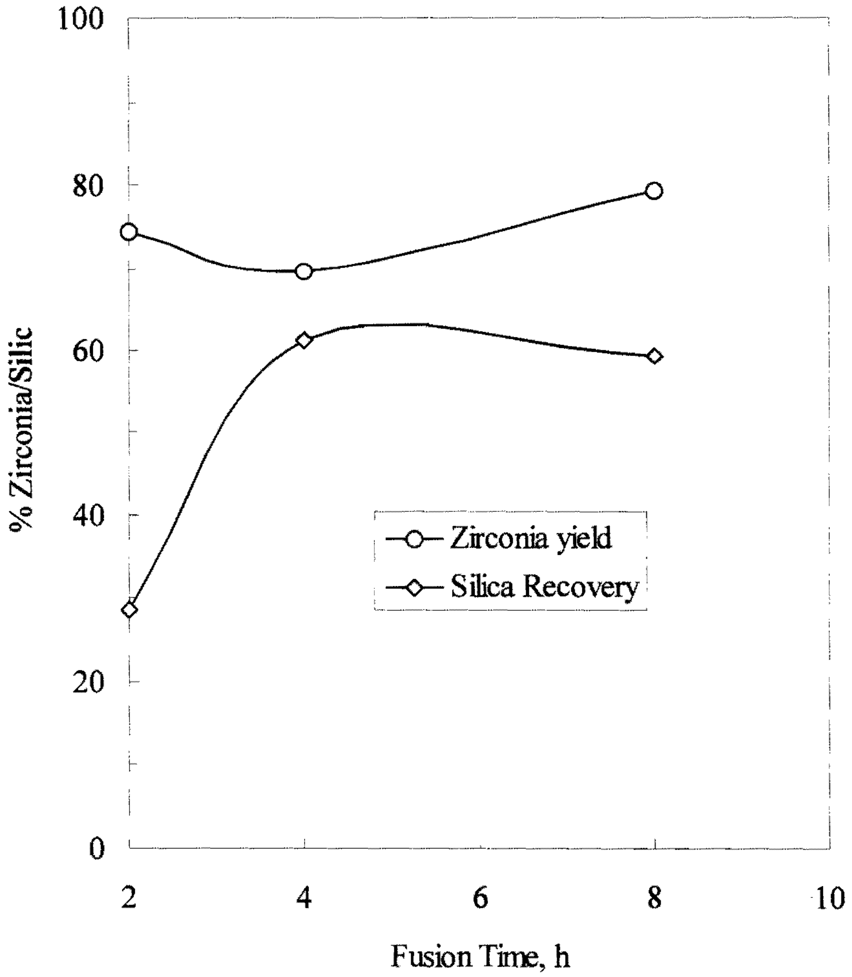

Figure 9.12: Zirconia yield and silica recovery obtained fusing a mole of zircon with four moles of sodium hydroxide at 850 °C

A reaction that may explain the concomitant decrease in zirconia yield at intermediate fusion times is presented in Scheme 9.5.

$$Na_2ZrSiO_5 + Na_2SiO_3 \rightarrow Na_4SiO_4 + ZrSiO_4$$

Scheme 9.5: Reaction that probably explains the drop in the zirconia yield

This reaction is consistent with the change in the product spectrum presented in Figure 9.10 and the sodium orthosilicate observed in the infrared spectra by Kwela [16]. He concluded that the sodium attacks the silica tetrahedra in preference to the zirconia.

9.5 Direct Zirconia Synthesis

Direct synthesis of zirconia from the AFDZ yielded a zirconia with purity as high as 87 %. This required fusion for 24 hours at 650 °C using 6 mol sodium hydroxide per mol of zircon. When fusing with 4 mol sodium hydroxide for 8 hours at 850 °C a yield of 79 % was obtained. A similar result was obtained using four moles of sodium hydroxide at 650 °C for 48 hours. The corresponding silica recoveries fell in a narrow range varying from a high of 65% to a low of 50%. However, 2-hours resulted in poor silica recovery. The low silica recoveries are attributed to formation of sodium zirconium silicate; it is not hydrolysed to hydrous zirconia by water alone.

10 CONCLUSIONS

The main objective of the present work was to optimise the alkali fusion step in the De Wet process for the recovery of zirconia from zircon sand. For this purpose experiments were conducted using various fusion times, fusion temperatures and stoichiometric ratios. Fusion times from 1 to 336 hours at temperatures between 600 °C and 850°C, at stoichiometric ratios ranging from 1 mol to 6 mol of sodium hydroxide per mol of zircon, were investigated.

The equilibrium phases at each temperature were determined using 336-hour fusions with intermittent milling of the reaction mixture. At temperatures below 650 °C, sodium zirconate (Na_2ZrO_3) is the equilibrium zirconium-containing phase. Above 700 °C, both sodium zirconate and sodium zirconium silicate (Na_2ZrSiO_5) are formed as products. As expected, for these temperatures, the product ratio depends on the reagent stoichiometry. Sodium zirconium silicate is almost the only zircon-based product that forms when 2 mol or less of NaOH are used per mol of zircon. Above this level, the sodium zirconate content in the reaction product increases with the NaOH:zircon mol ratio.

Thus, at low fusion temperatures, the zirconium-containing product is sodium zirconate, independent of the reagent mol ratio. At high temperatures and low mol ratios, the main phase formed is sodium zirconium silicate, while above mol ratios of 4:1 it is sodium zirconate. Sodium metasilicate is the only crystalline silicate phase formed after a long period of fusion, independently of the stoichiometry of the reaction, provided it is below a ratio of 4:1 (NaOH: $ZrSiO_4$).

Both equilibrium products are suitable for the recovery of zirconia from zircon sands. In water, sodium zirconate hydrolyses directly to form hydrous zirconia. Sodium zirconium silicate is hydrolysed only in the presence of a dilute acid, e.g. hydrochloric acid, yielding hydrous zirconia as well as hydrous silica. The liberation of zirconia from zircon via sodium zirconate requires 4 mol NaOH per mol of zircon. In contrast, the formation of sodium zirconium silicate requires only 2 mol of NaOH per mol of zircon. However, in the sodium zirconate route, the sodium can be recovered from the wash water as saleable sodium silicate. With the sodium zirconium silicate route, the sodium is not recovered. Additional acid reagent is consumed during hydrolysis and a salt-containing waste stream results. Optimum zirconia yields and minimum waste-stream generation are achieved when 2 mol of NaOH are fused with 1 mol of $ZrSiO_4$ at 850 °C for 2 hours.

In general, the fusion product contains both compounds. From a practical point of view, short fusion times are preferable. A 1-hour fusion does not produce acceptable conversion. Fusions conducted at 850 °C with a 2:1 reagent mol ratio showed a maximum zirconia yield at 2 hours. This is attributed to a high proportion of Na_2ZrSiO_5 in the product spectrum. The drop in zirconia yield might be caused by a disproportional reaction between Na_2ZrSiO_5 and Na_2SiO_3 that reconstitutes zircon.

When NaOH:zircon mol ratios exceeding 4:1 are fused, Na_2ZrO_3 is the dominant product. The silica is present as ortho- and meta-silicates and can be leached with water. In principle, exhaustive water leaching also leads to the hydrolysis of the sodium zirconate. In practice, it needs to be accelerated by adding dilute acid. After leaching, the residue should essentially consist of hydrated zirconia. This can be fired to produce zirconia directly. The best results were obtained with a 24-hour fusion and a 6:1 stoichiometric mol ratio. This reaction produced zirconia at 86,5% purity. Reducing the stoichiometry to 4:1 yielded, under similar reaction conditions, zirconia with a purity of 84%. In both cases, the impurity was zircon.

Attempts to synthesise zirconia directly from AFDZ only yielded impure product. High yields required high sodium hydroxide to zircon mol ratios. A product containing 79% zirconia was obtained by fusing for 24 hours at 650 °C using a 6:1 mol ratio. The corresponding silica recovery was always lower than the zirconia purity owing to the formation of sodium zirconium silicate.

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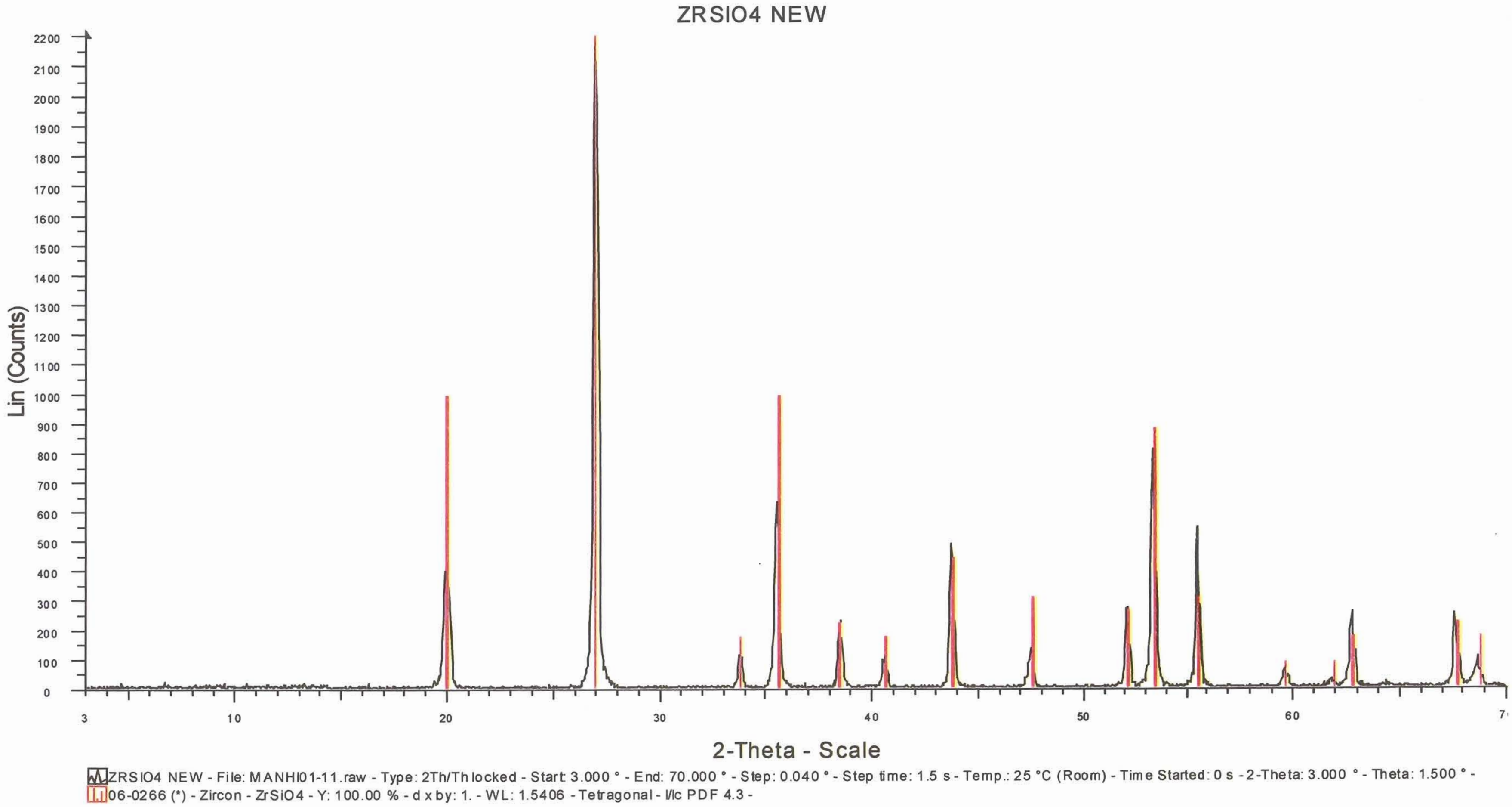


Figure 8.1: XRD spectrum of zircon

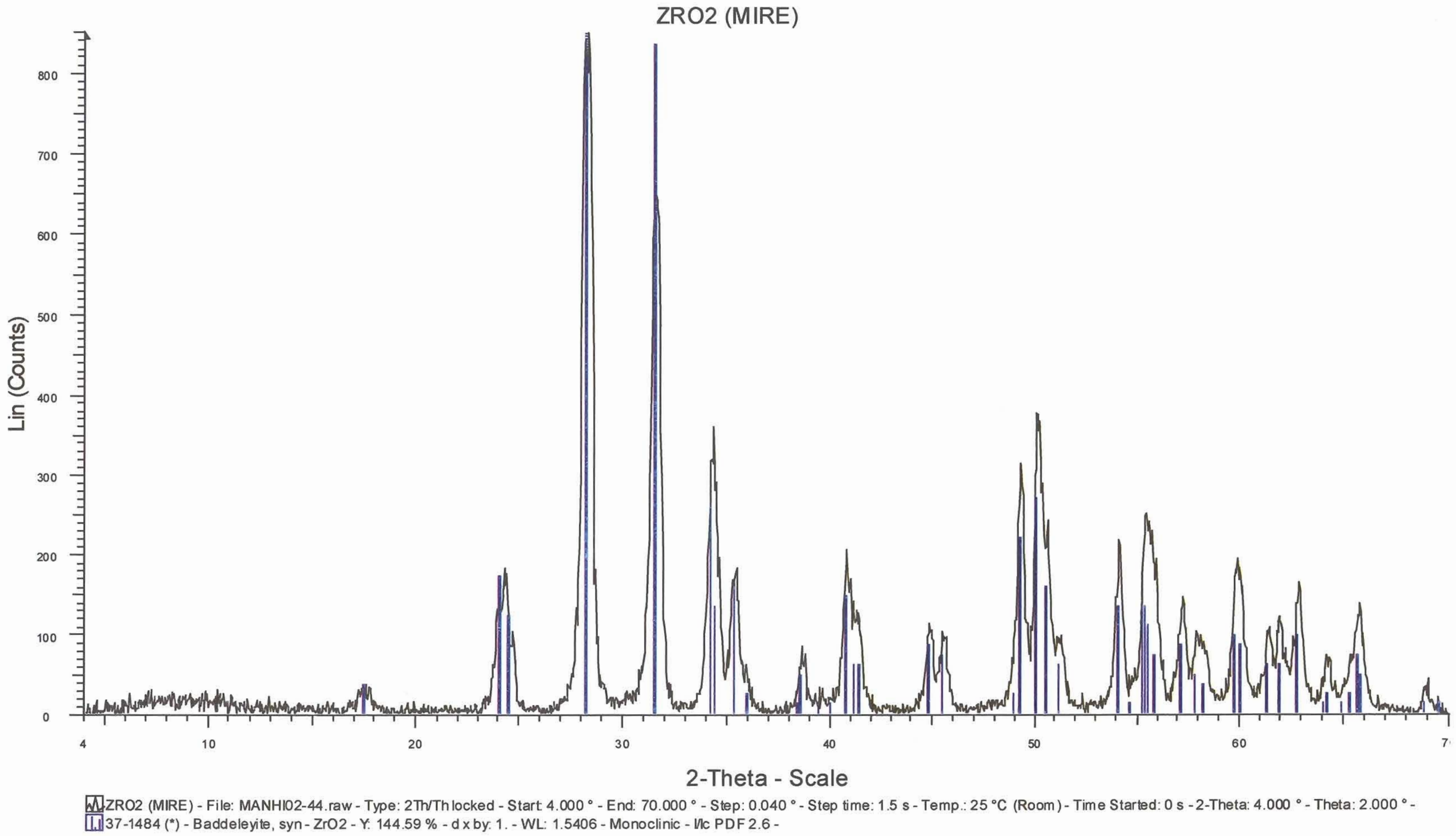
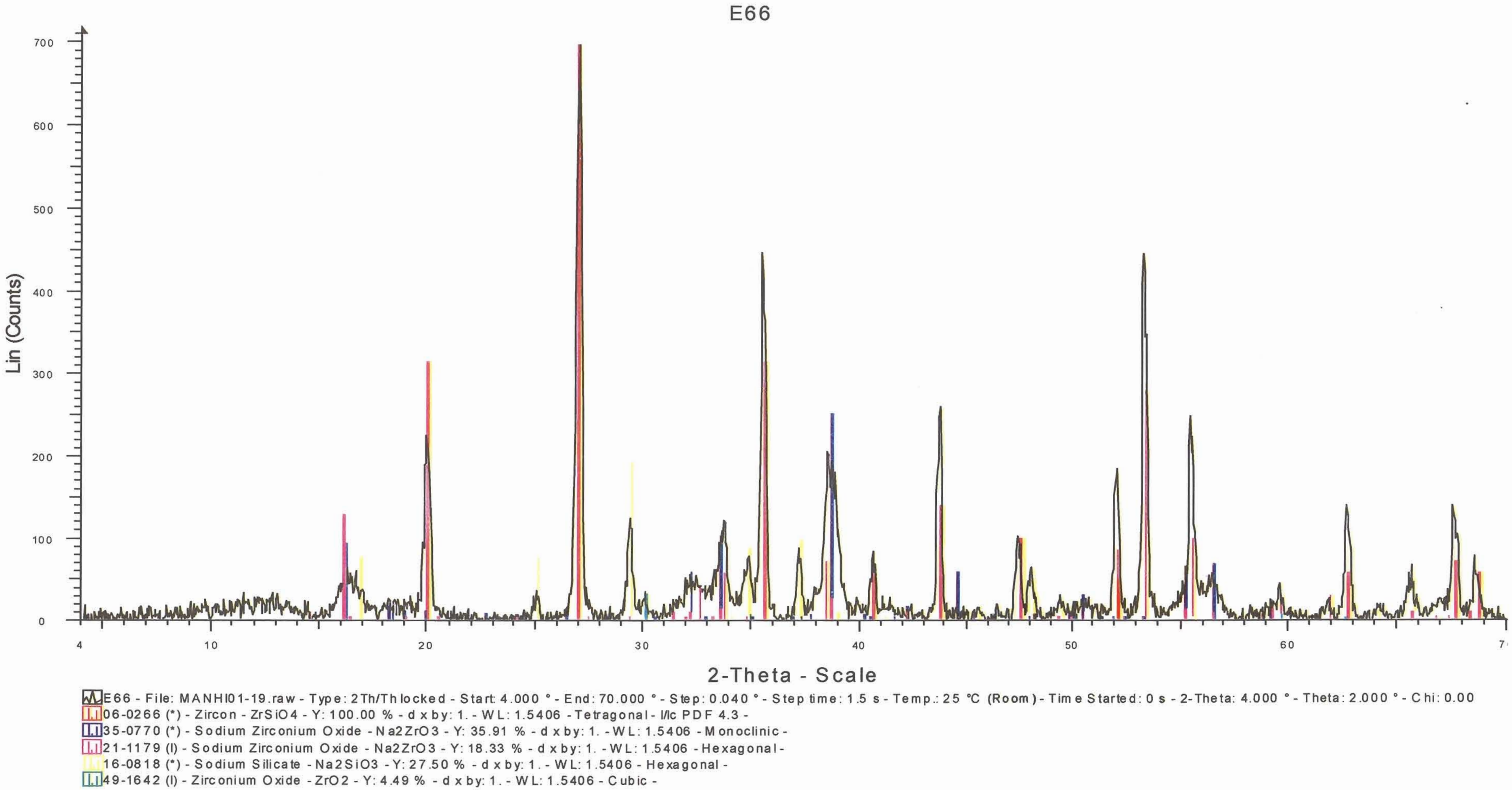
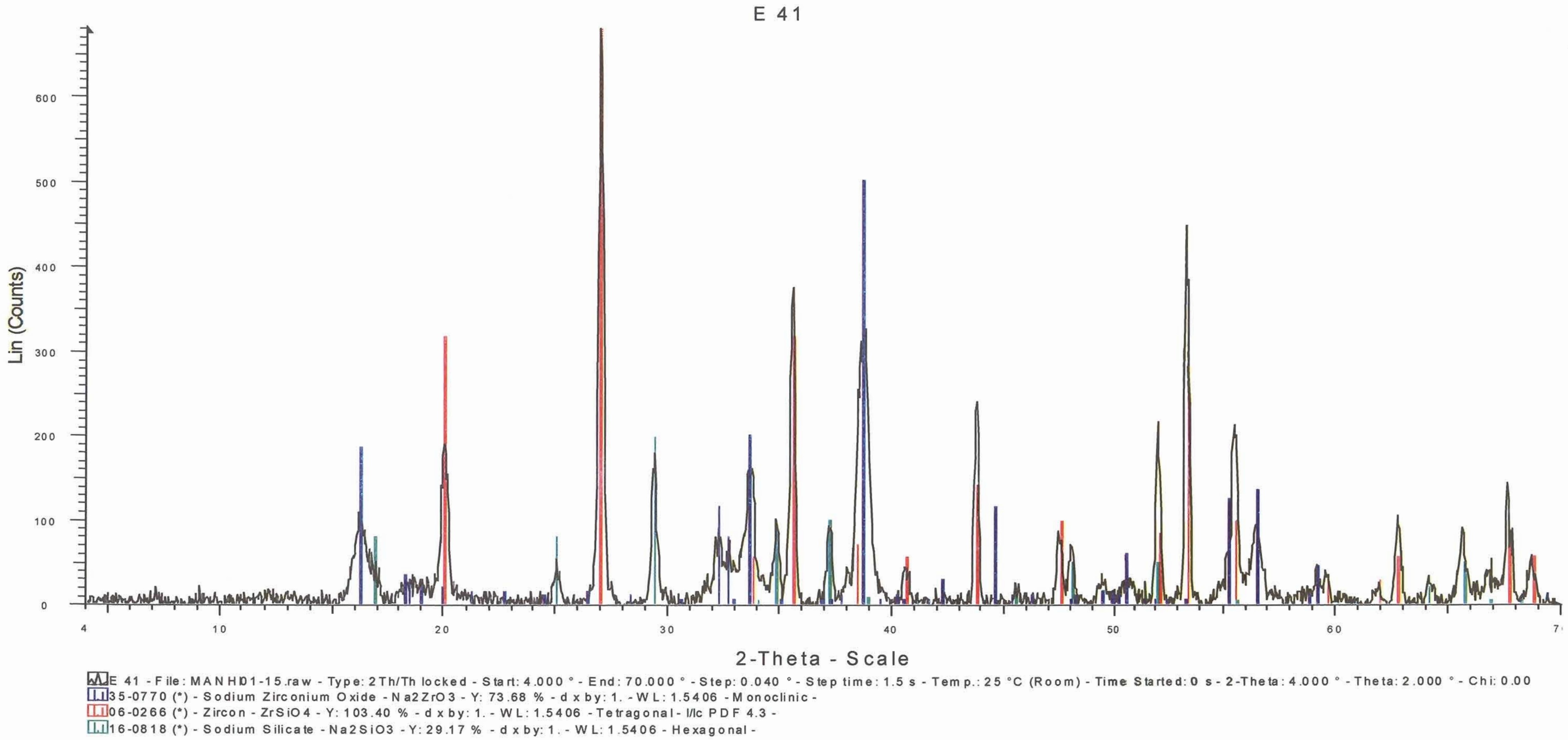


Figure 8.2: XRD-spectrum of pure zirconia.

Appendix A

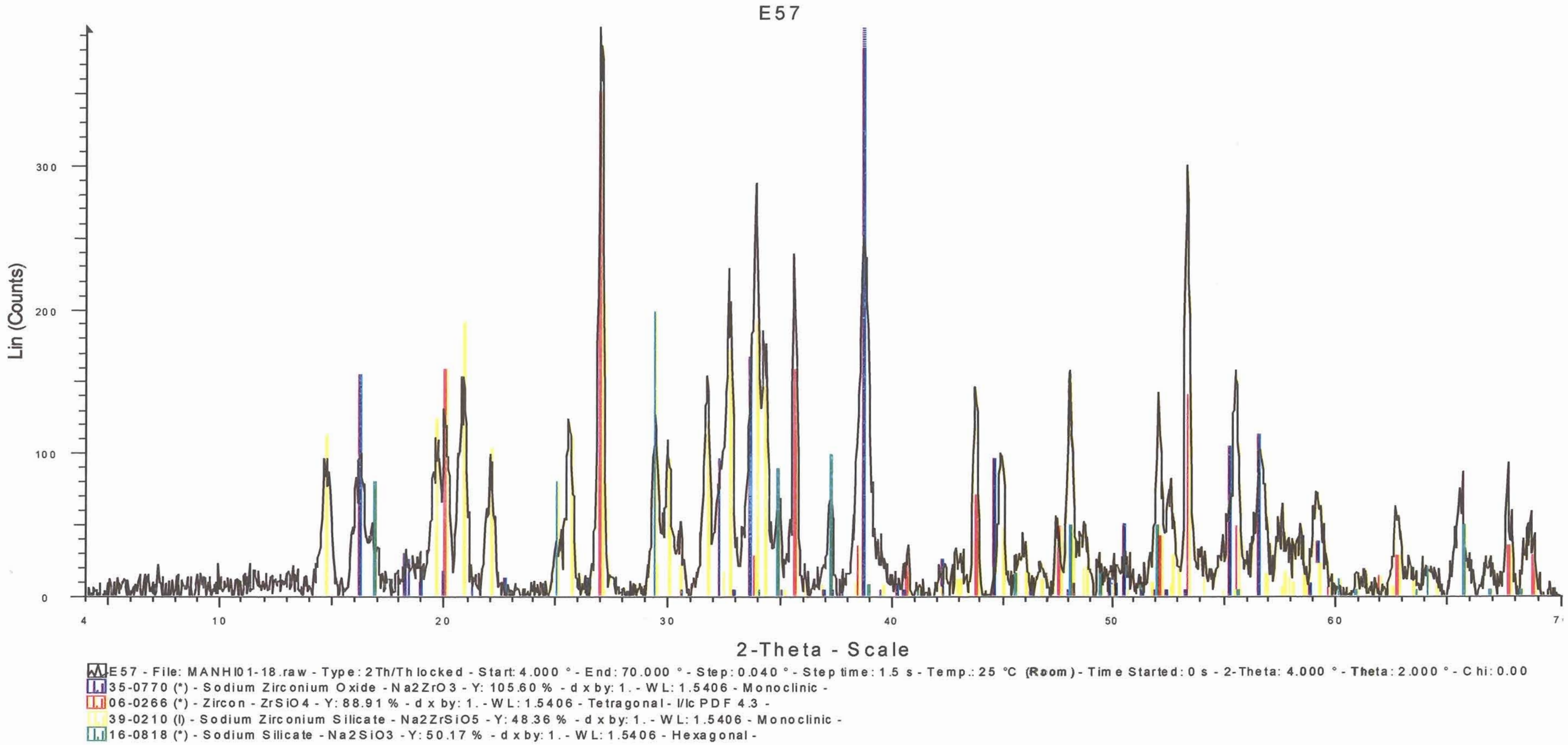


Spectrum 3: XRD spectrum of zircon alkali fused. One mole of zircon d ≈ 9.0 μm was fused with two moles of sodium hydroxide at 600ºC for 336 hours with intermediate milling after every 24 hours.

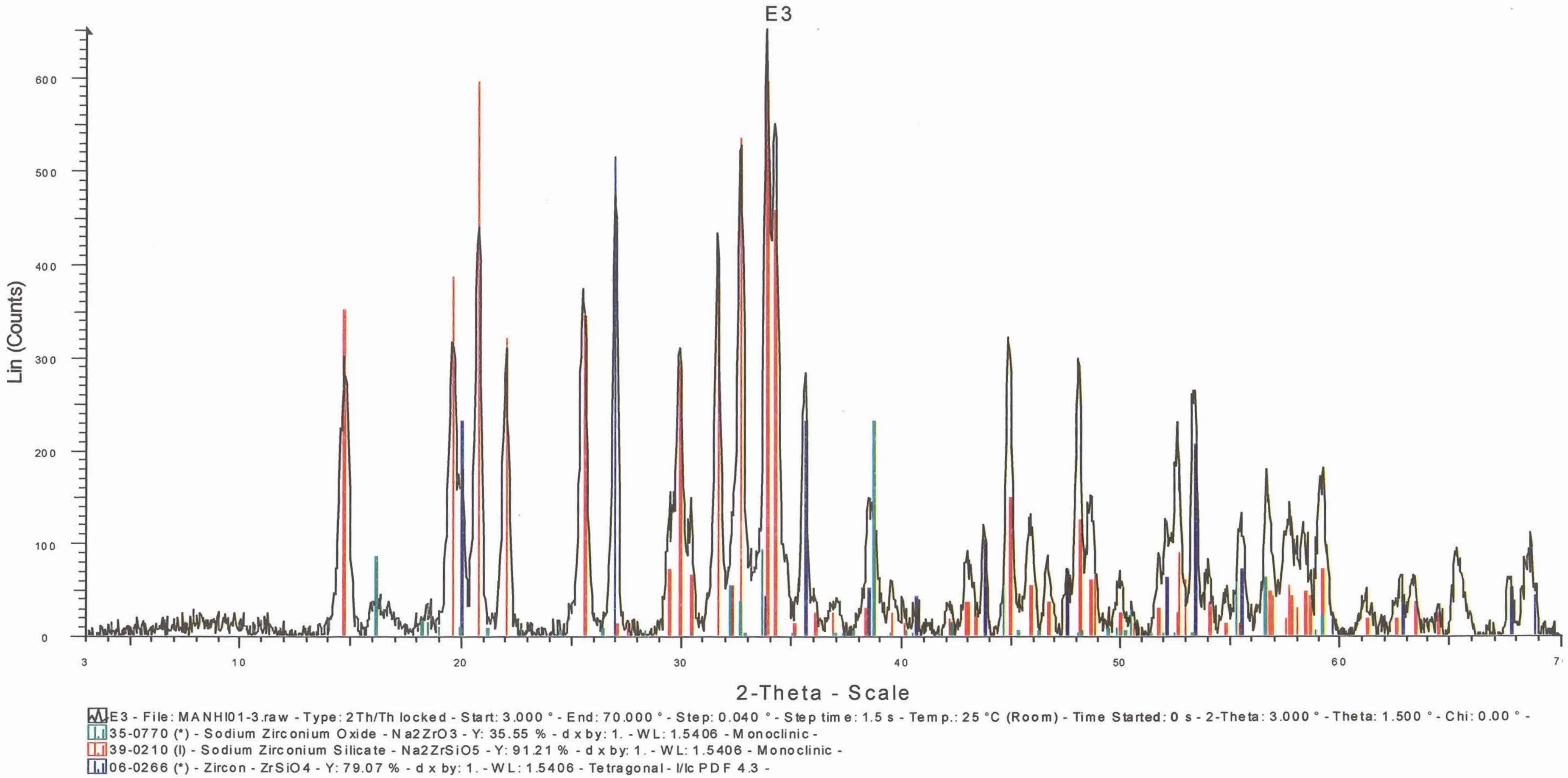


Spectrum 4: XRD spectrum of zircon alkali fused. A mole of zircon d ≈ 9.0 µm was fused with two moles of sodium hydroxide at 650°C for 336 hours with intermediate milling after every 24 hours.

Appendix A

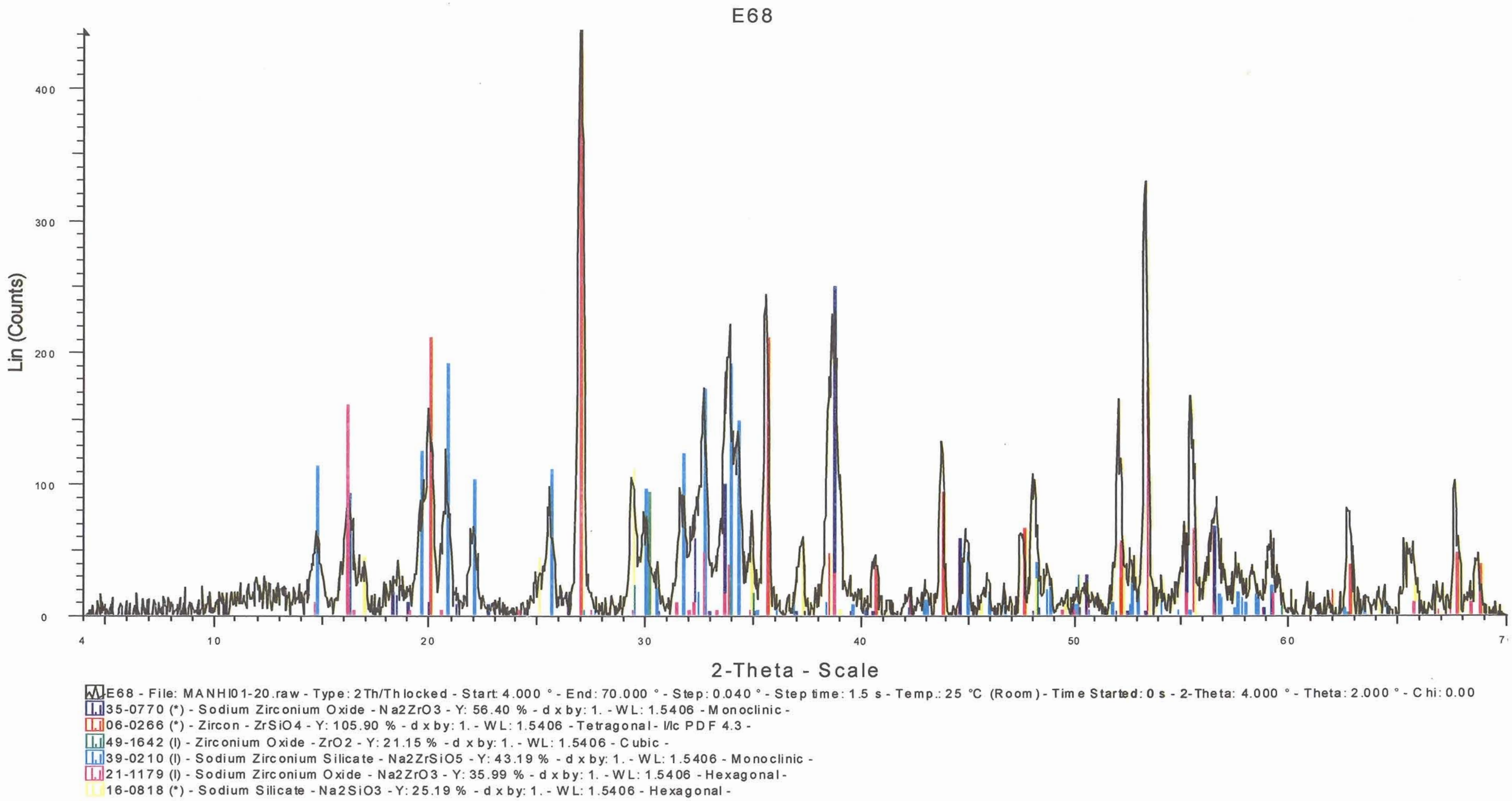


Spectrum 5: XRD spectrum of zircon alkali fused. A mole of zircon d ≈ 9.0 μm was fused with two moles of sodium hydroxide at 700ºC for 336 hours with intermediate milling after every 24 hours.



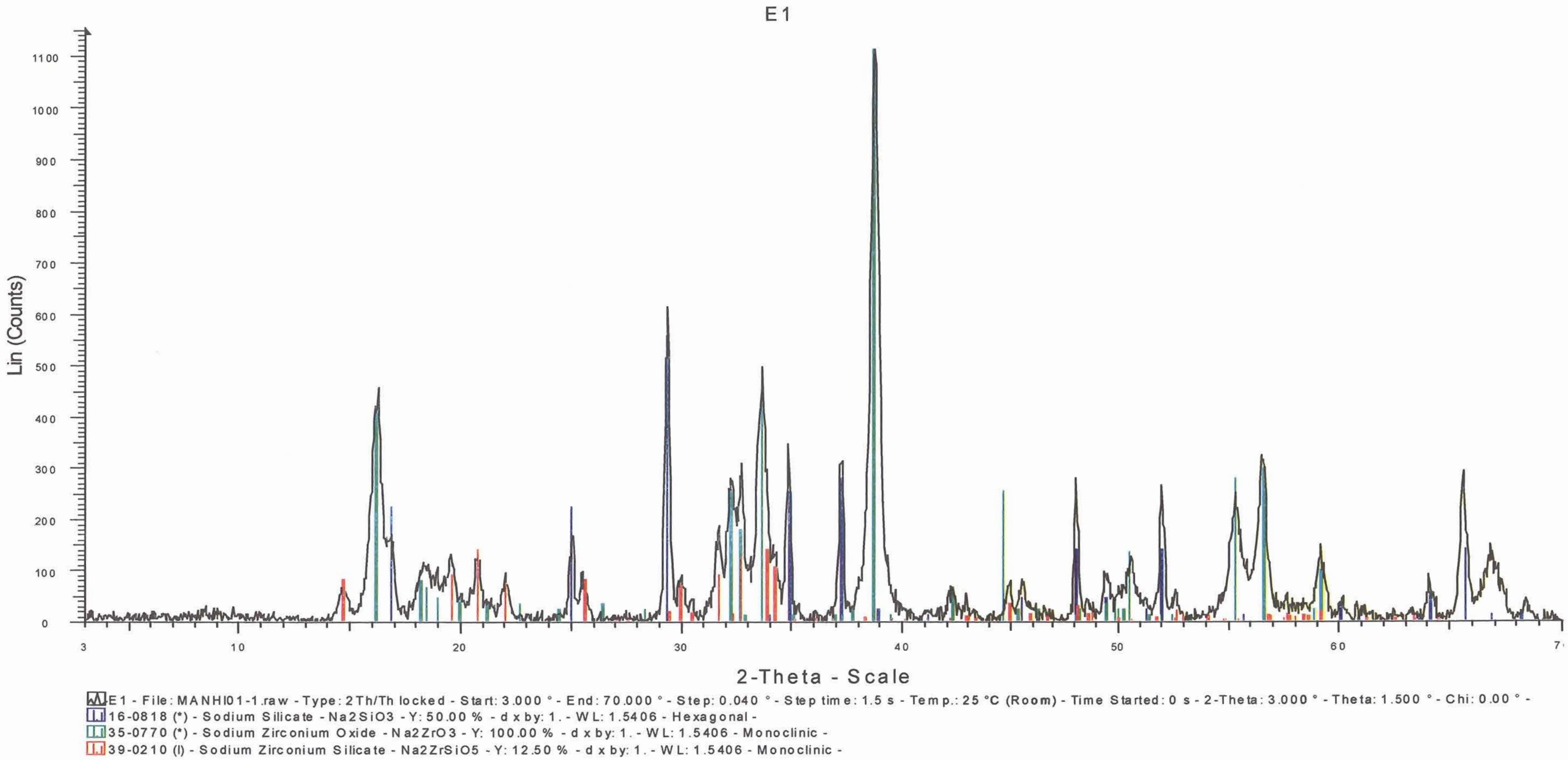
Spectrum 6: XRD spectrum of zircon alkali fused. A mole of zircon d ≈ 9.0 µm was fused with one mole of sodium hydroxide at 750°C for 336 hours with intermediate milling after every 24 hours.

Appendix A



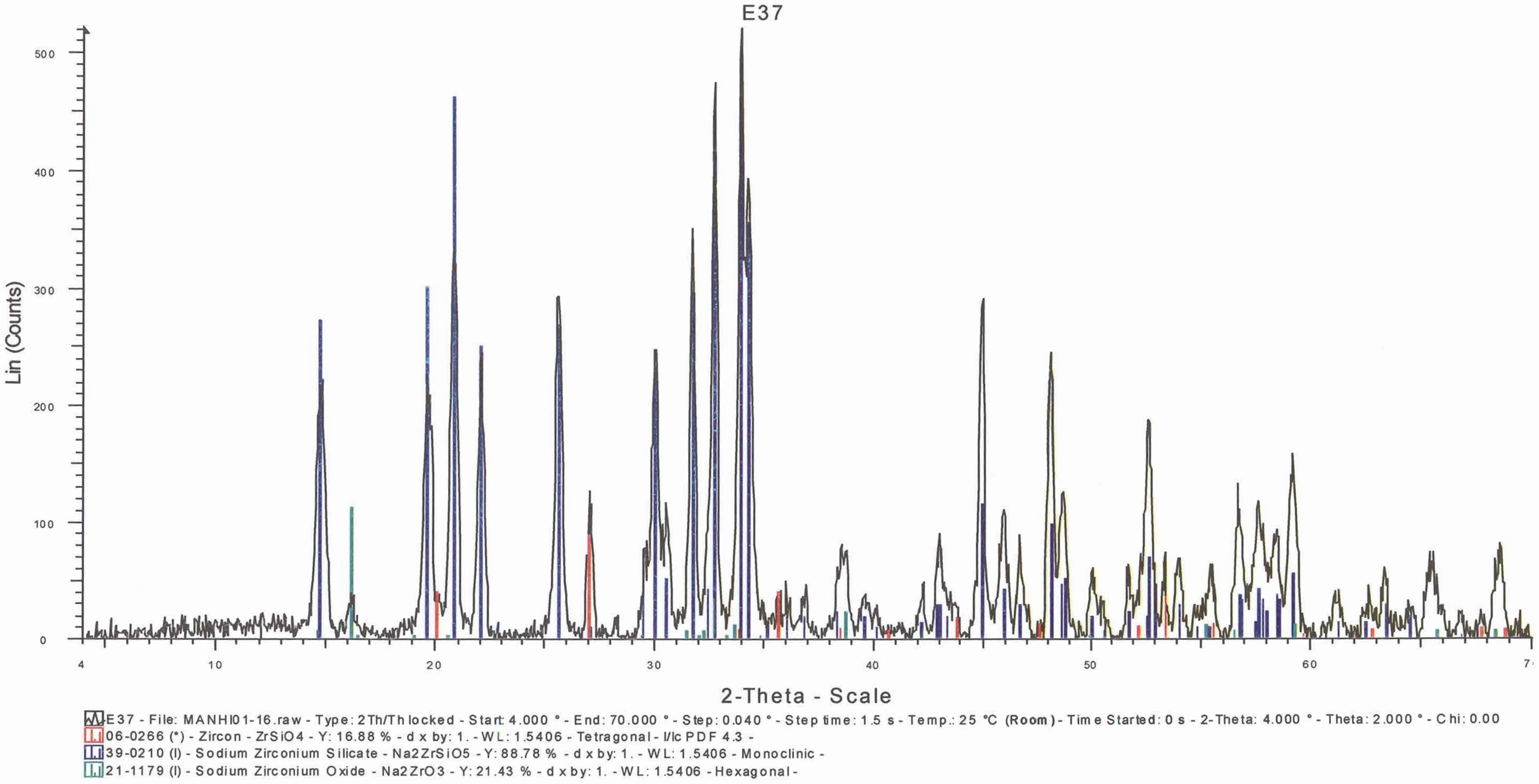
Spectrum 7: XRD spectrum of zircon alkali fused. A mole of zircon d ≈ 9.0 μm was fused with two moles of sodium hydroxide at 750ºC for 336 hours with intermediate milling after every 24 hours.

Appendix A



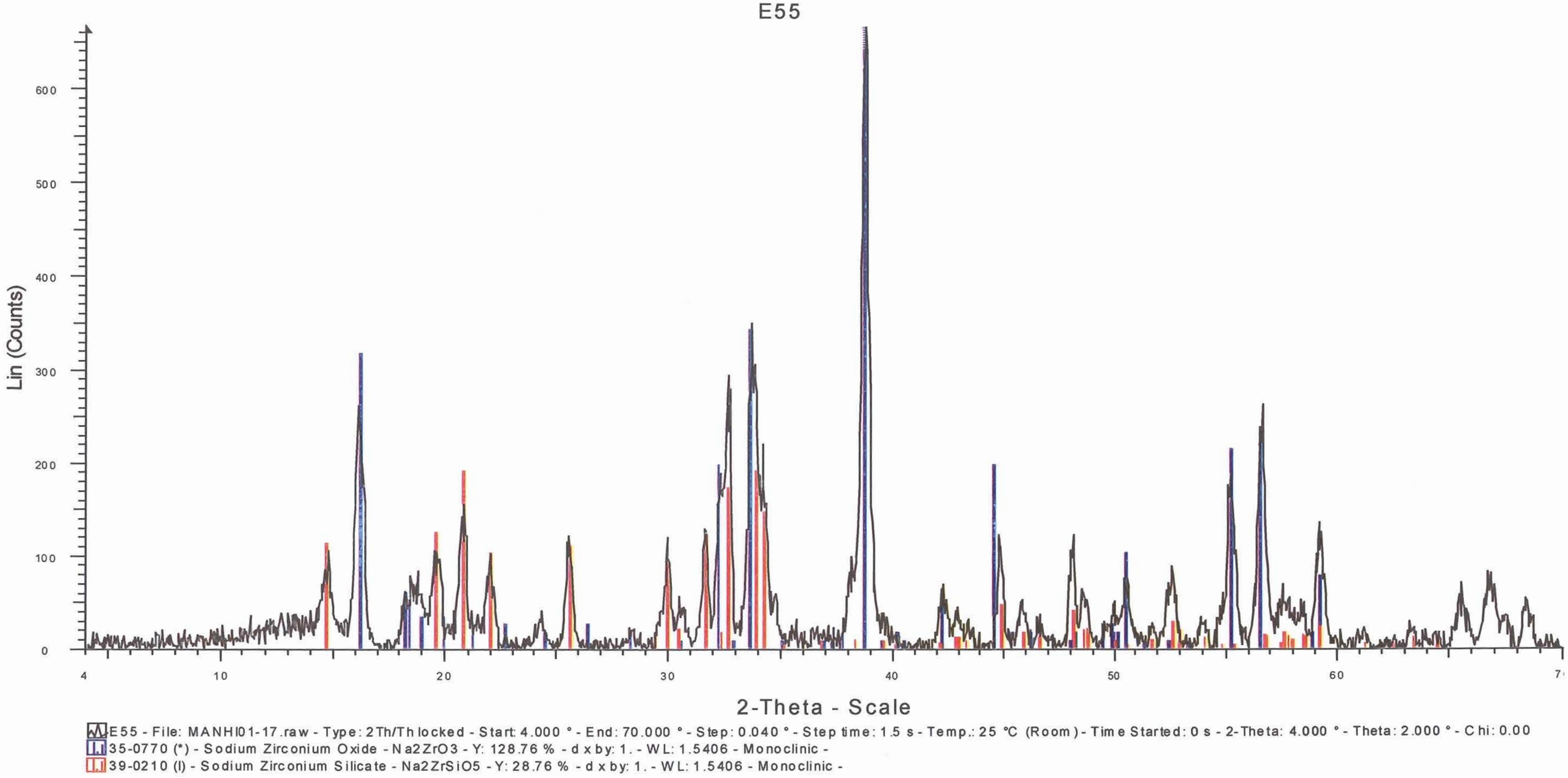
Spectrum 8: XRD spectrum of zircon alkali fused. A mole of zircon d ≈ 9.0 µm was fused with four moles of sodium hydroxide at 750ºC for 336 hours with intermediate milling after every 24 hours.

Appendix A



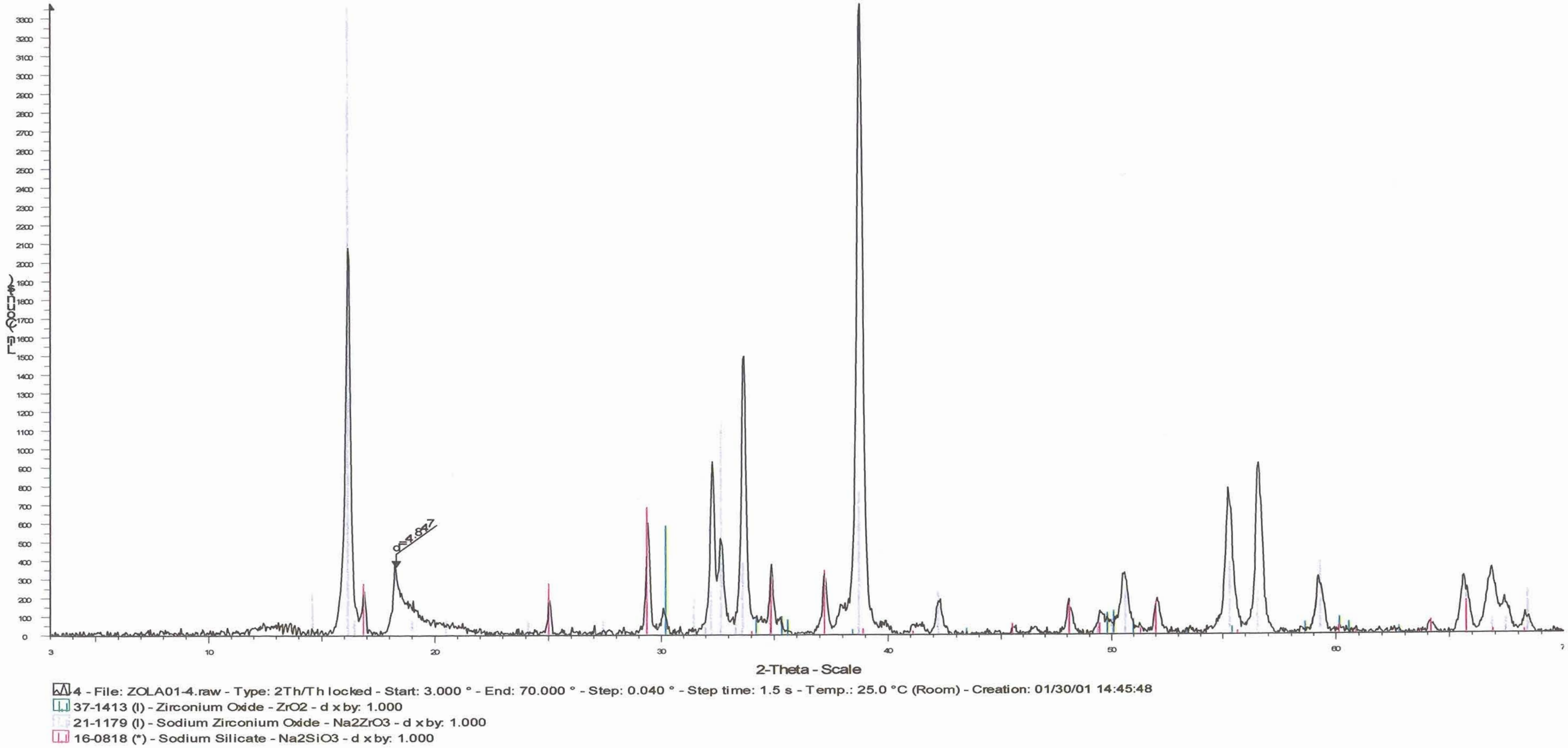
Spectrum 9: XRD spectrum of zircon alkali fused. A mole of zircon d ≈ 9.0 µm was fused with two moles of sodium hydroxide at 850°C for 336 hours with intermediate milling every 24 hours.

Appendix A



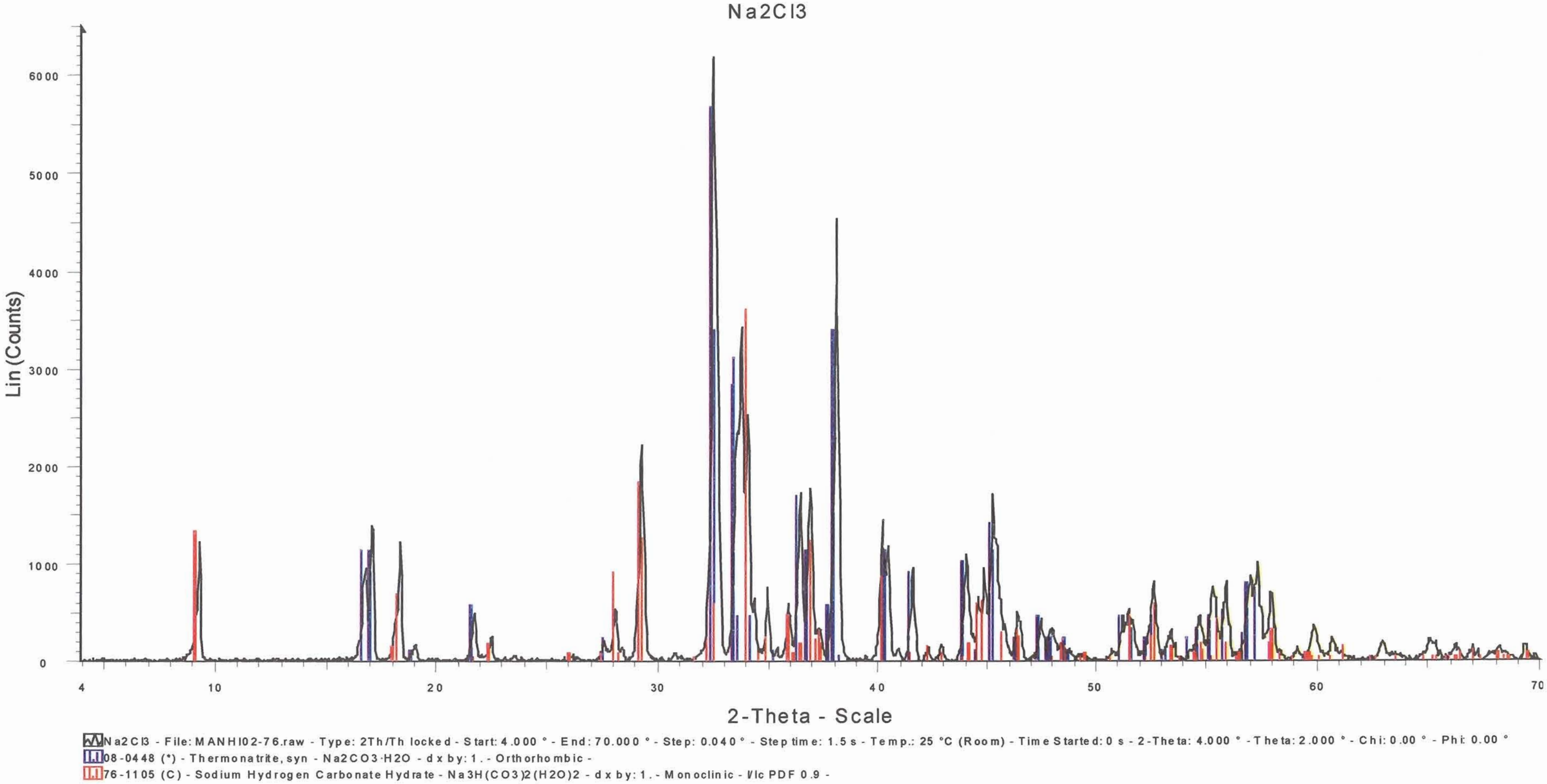
Spectrum 10: XRD spectrum of zircon alkali fused. A mole of zircon d ≈ 9.0 μm was fused with four moles of sodium hydroxide at 850°C for 336 hours with intermediate milling every 24 hours.

Appendix A



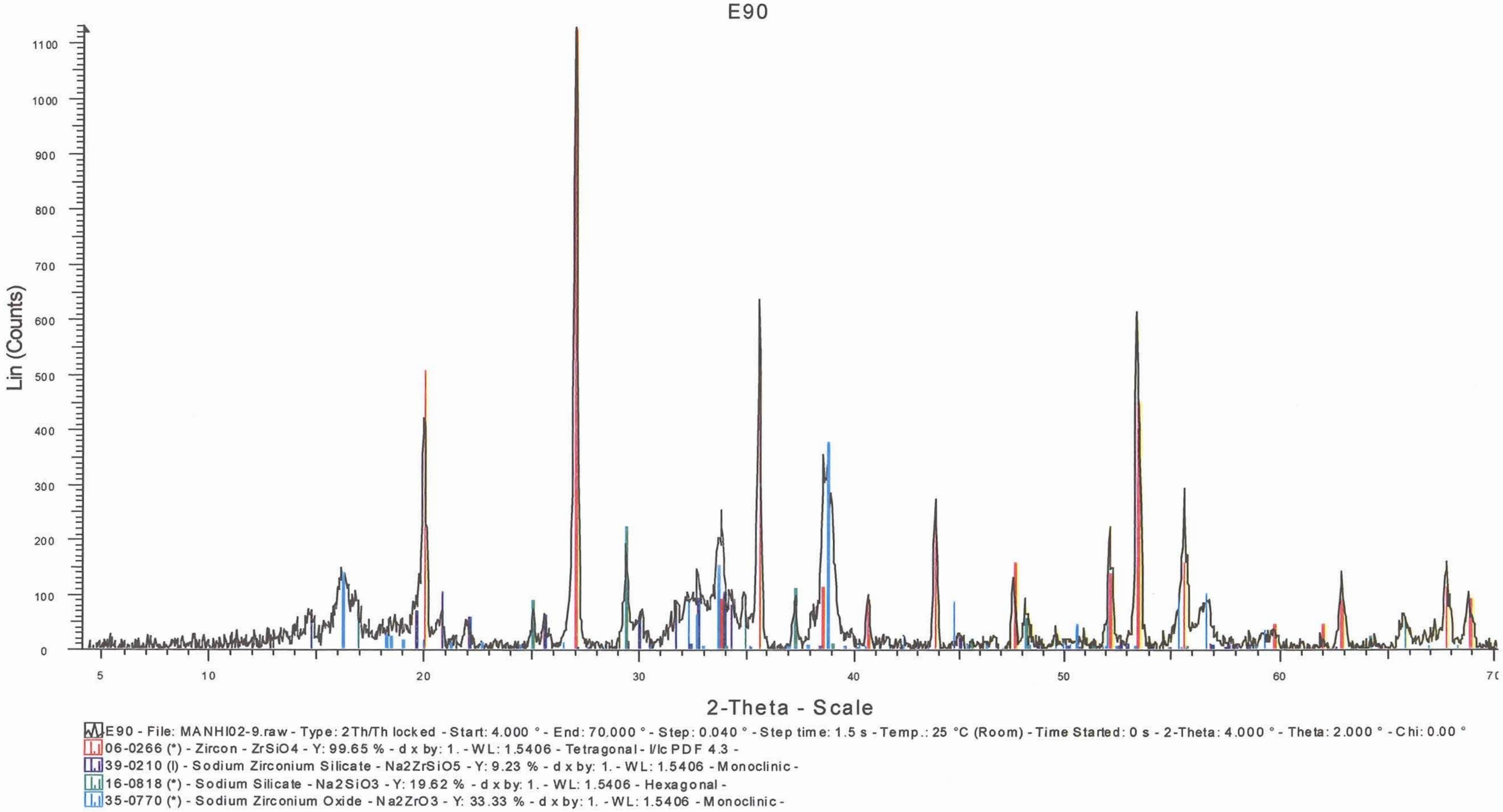
Spectrum 11: XRD spectrum of zircon alkali fused. A mole of zircon d ≈ 9.0 μm was fused with six moles of sodium hydroxide at 850°C for 336 hours with intermediate milling every 24 hours [16].

Appendix A



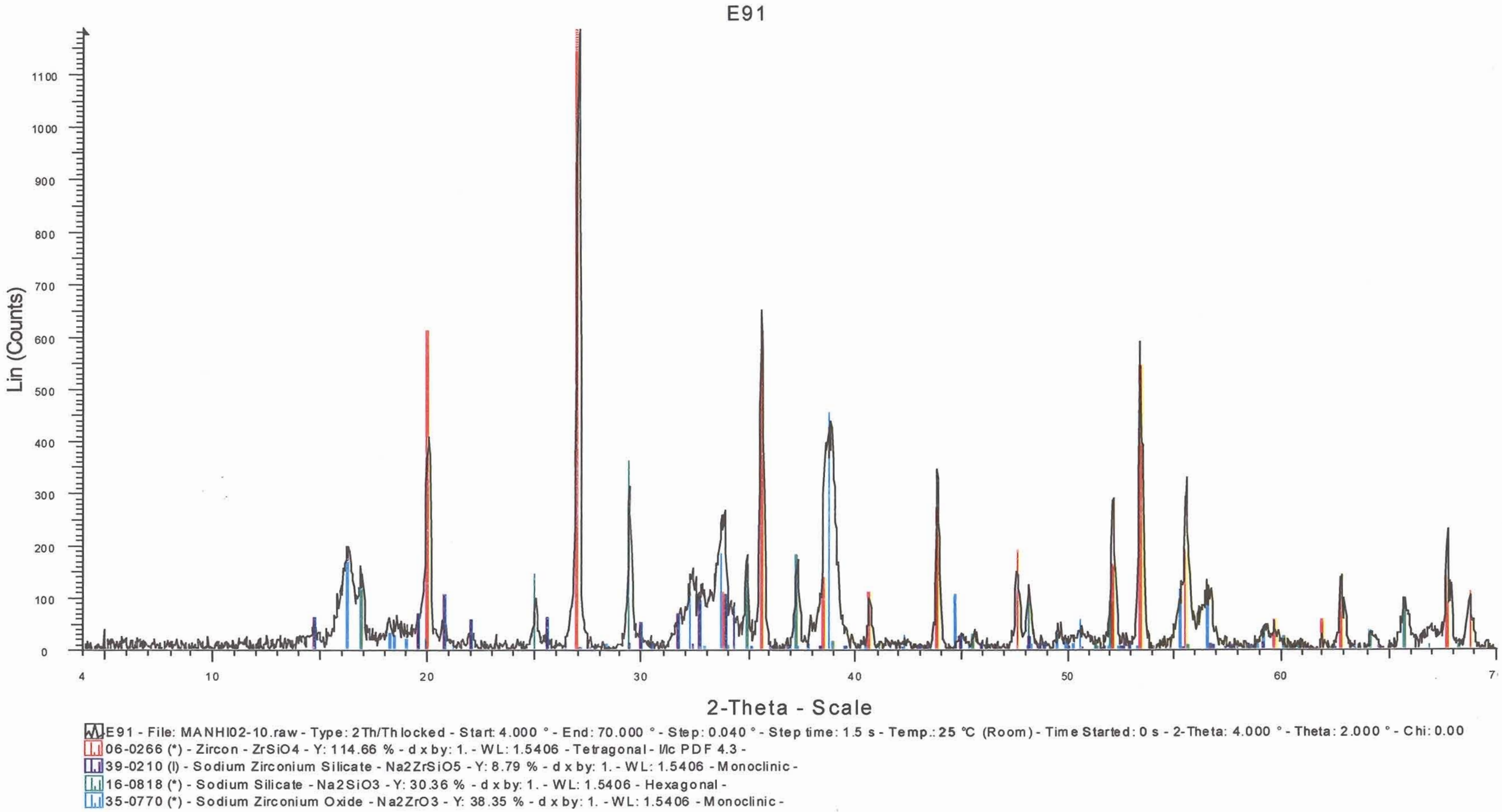
Spectrum 12: XRD spectrum of sodium carbonate.

Appendix A



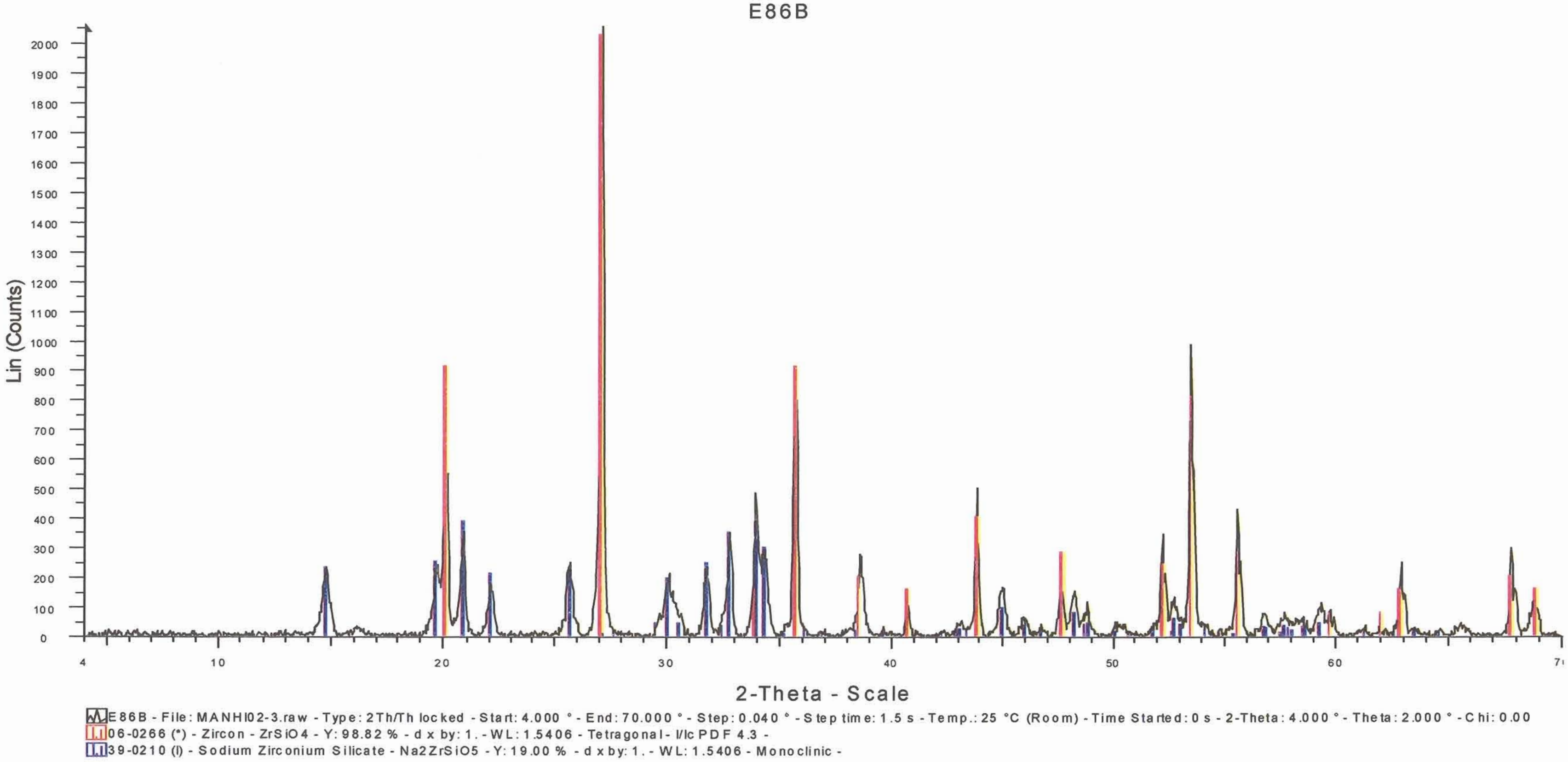
Spectrum 13: XRD spectrum of zircon alkali fused. A mole of zircon d ≈ 9.0 μm was fused with two moles of sodium hydroxide at 850°C for one hour without intermediate milling.

Appendix A

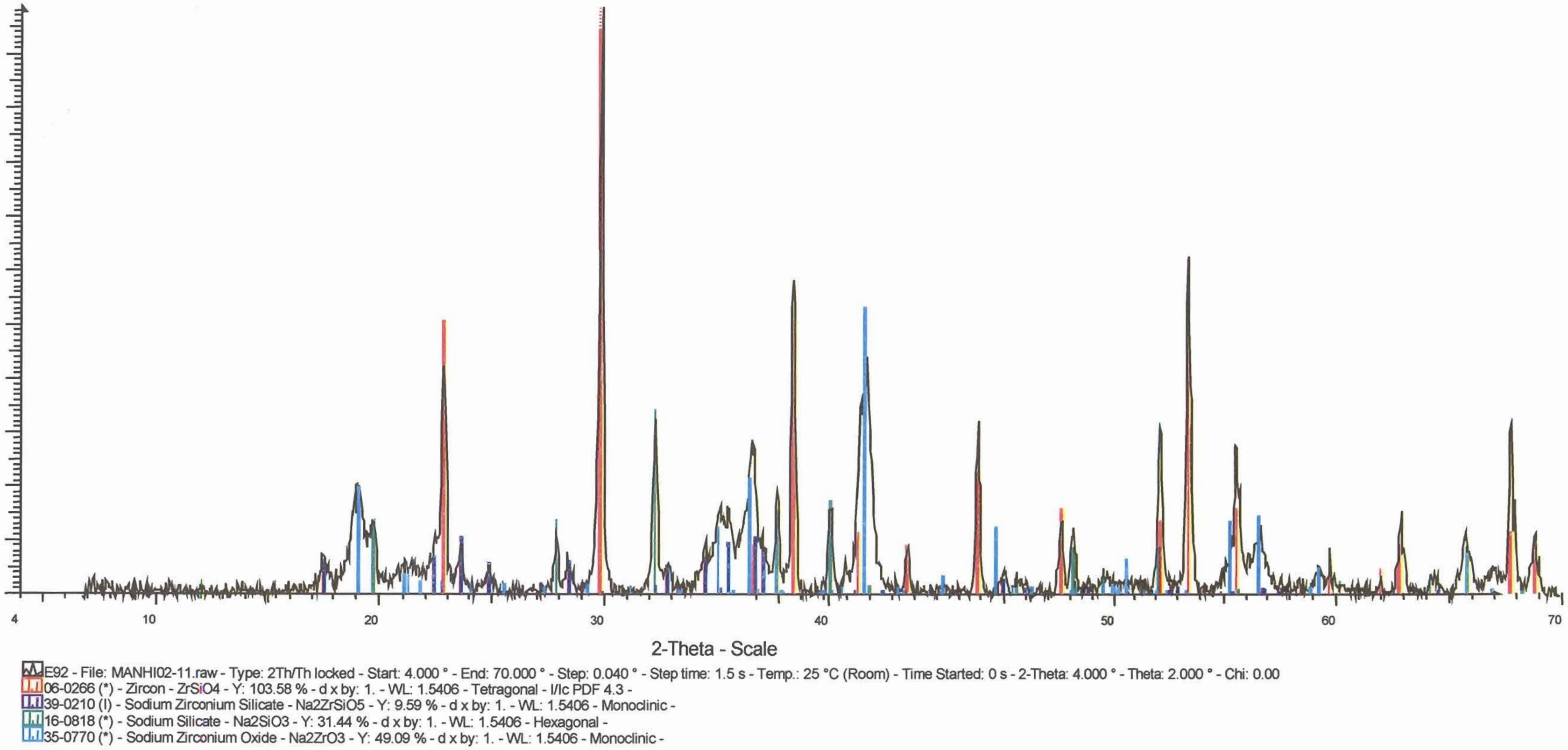


Spectrum 14: XRD spectrum of zircon alkali fused. A mole of zircon d ≈ 9.0 μm was fused with two moles of sodium hydroxide at 850°C for one hour with intermediate milling.

Appendix A

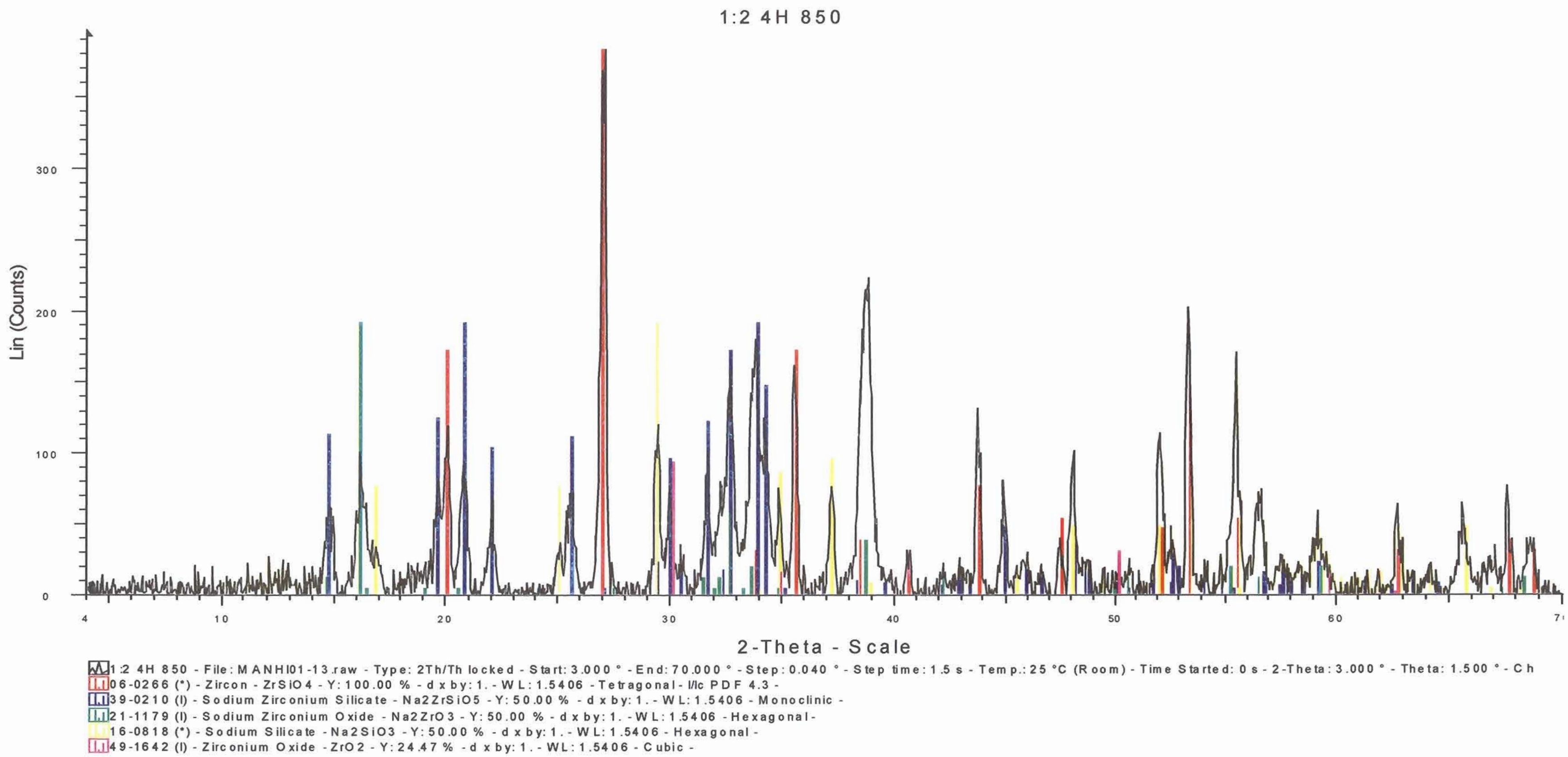


Spectrum 15: XRD spectrum of zircon alkali fused. A mole of zircon d ≈ 9.0 μm was fused with one mole of sodium hydroxide at 850°C for 48 hours with intermediate milling.



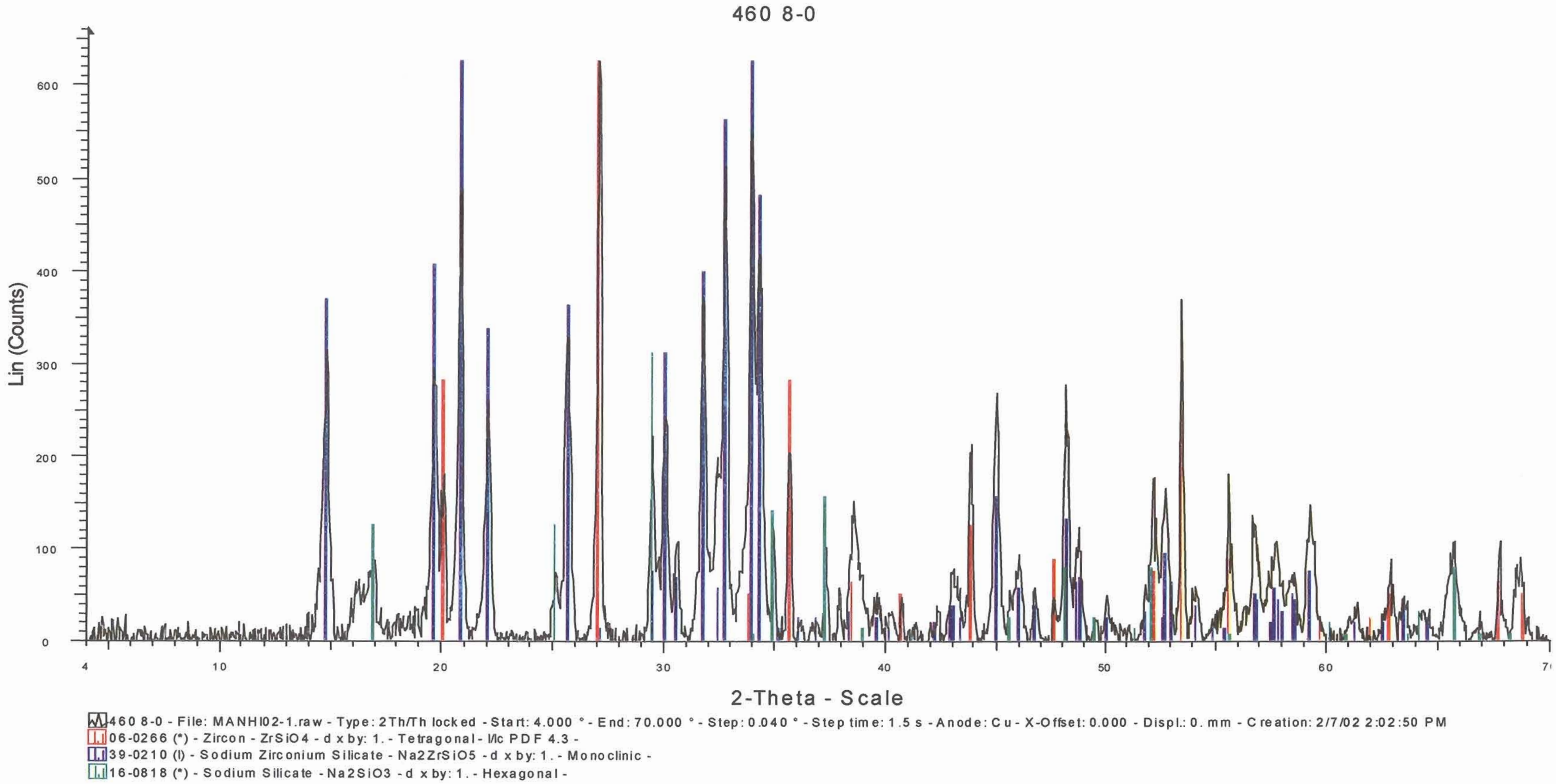
Spectrum 16: XRD spectrum of zircon alkali fused. A mole of zircon d ≈ 9.0 µm was fused with two moles of sodium hydroxide at 850°C for two hours with intermediate milling at one hour.

Appendix A



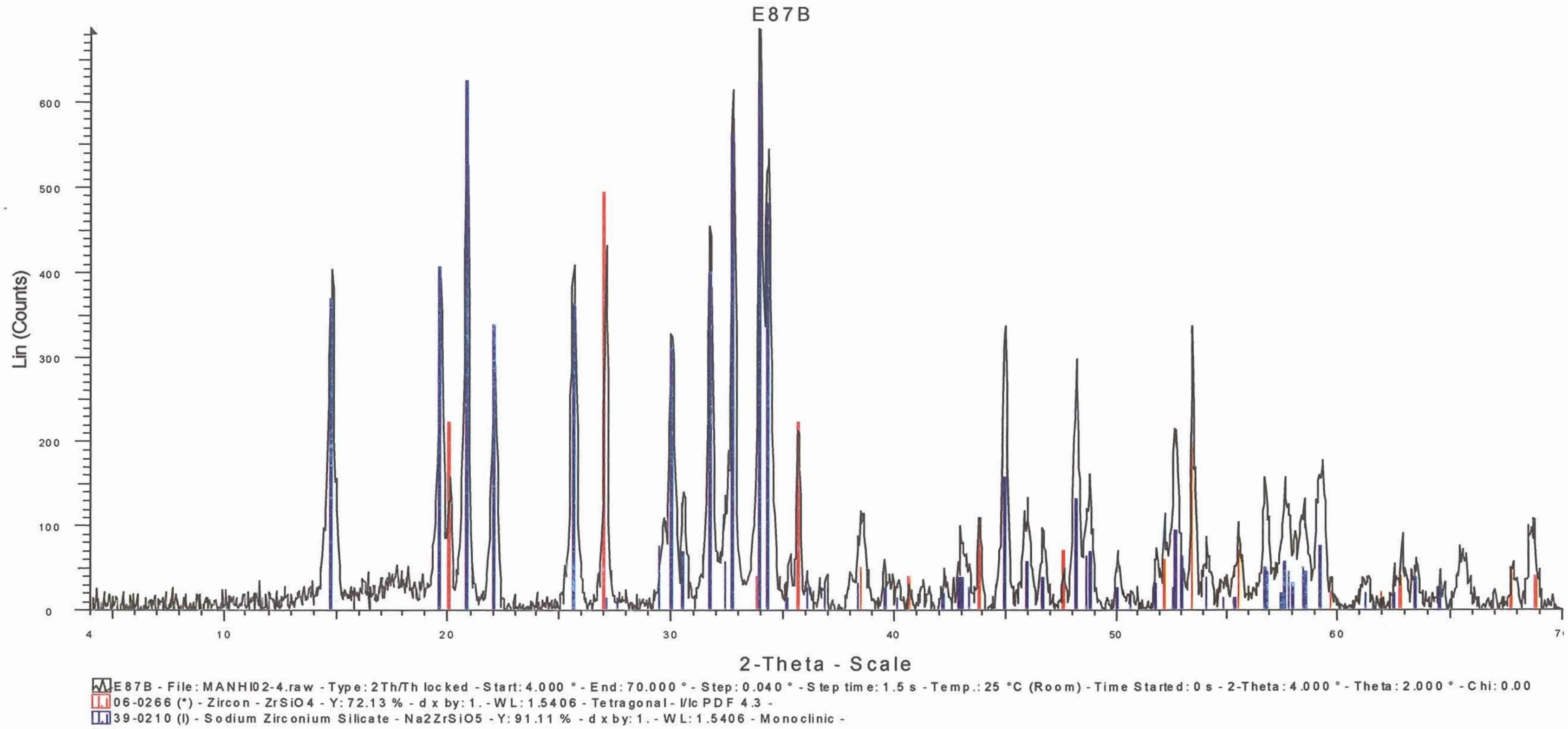
Spectrum 17: XRD spectrum of zircon alkali fused. A mole of zircon d ≈ 9.0 μm was fused with two moles of sodium hydroxide at 850°C for four hours with intermediate milling at two hours.

Appendix A

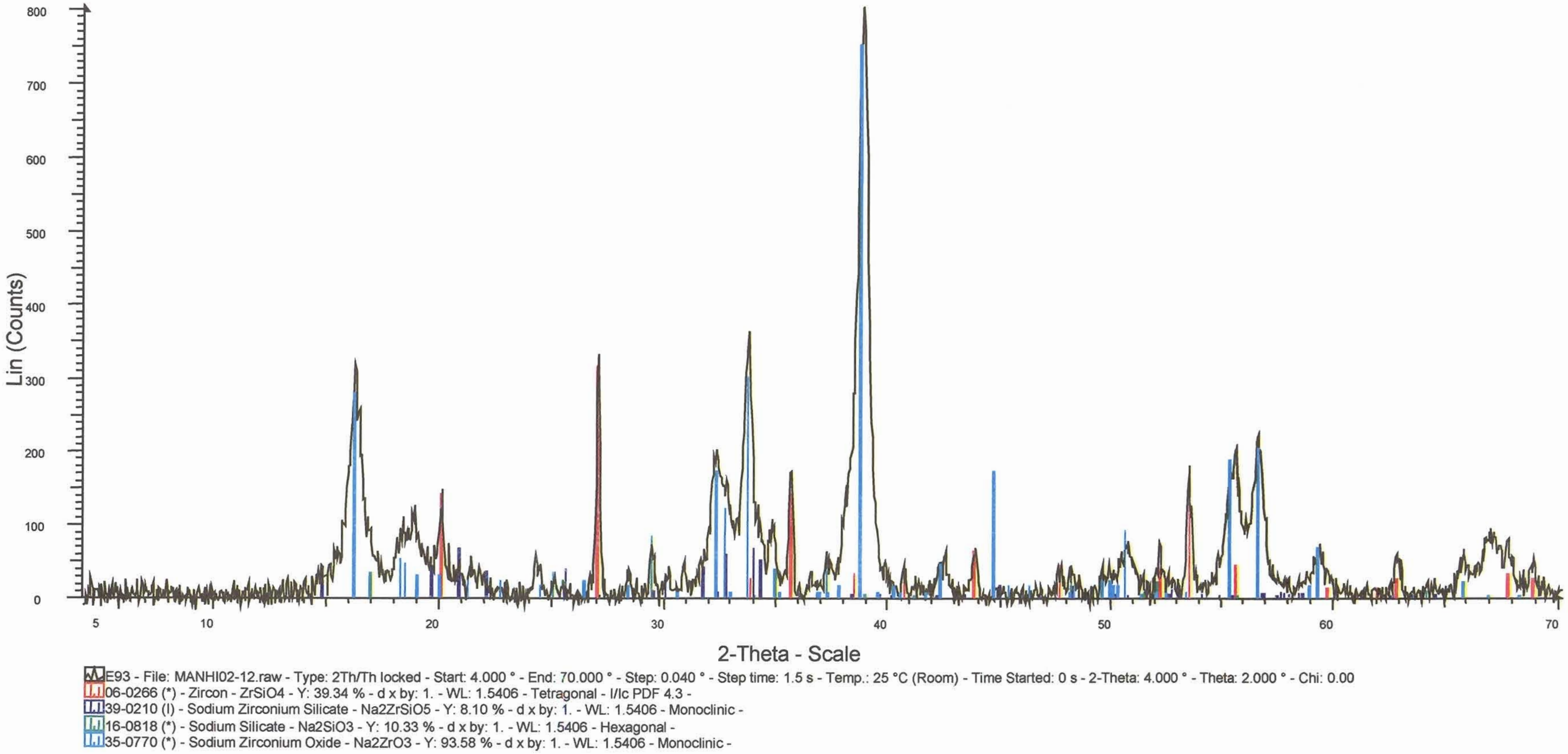


Spectrum 18: XRD spectrum of zircon alkali fused. A mole of zircon d ≈ 9.0 µm was fused with two moles of sodium hydroxide at 850°C for 24 hours with intermediate milling.

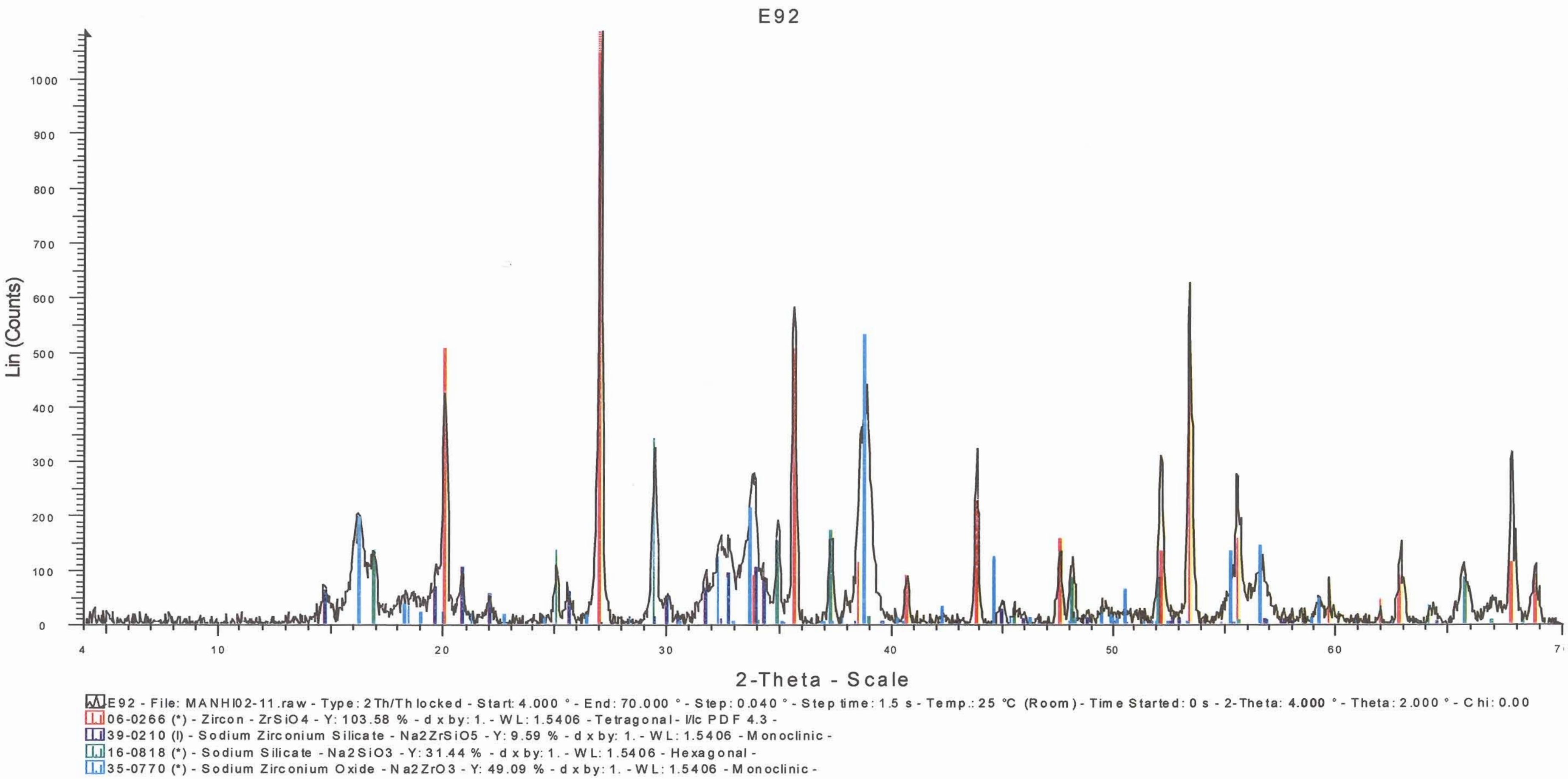
Appendix A



Spectrum 19: XRD spectrum of zircon alkali fused. A mole of zircon d ≈ 9.0 μm was fused with two moles of sodium hydroxide at 850°C for 48 hours with intermediate milling.

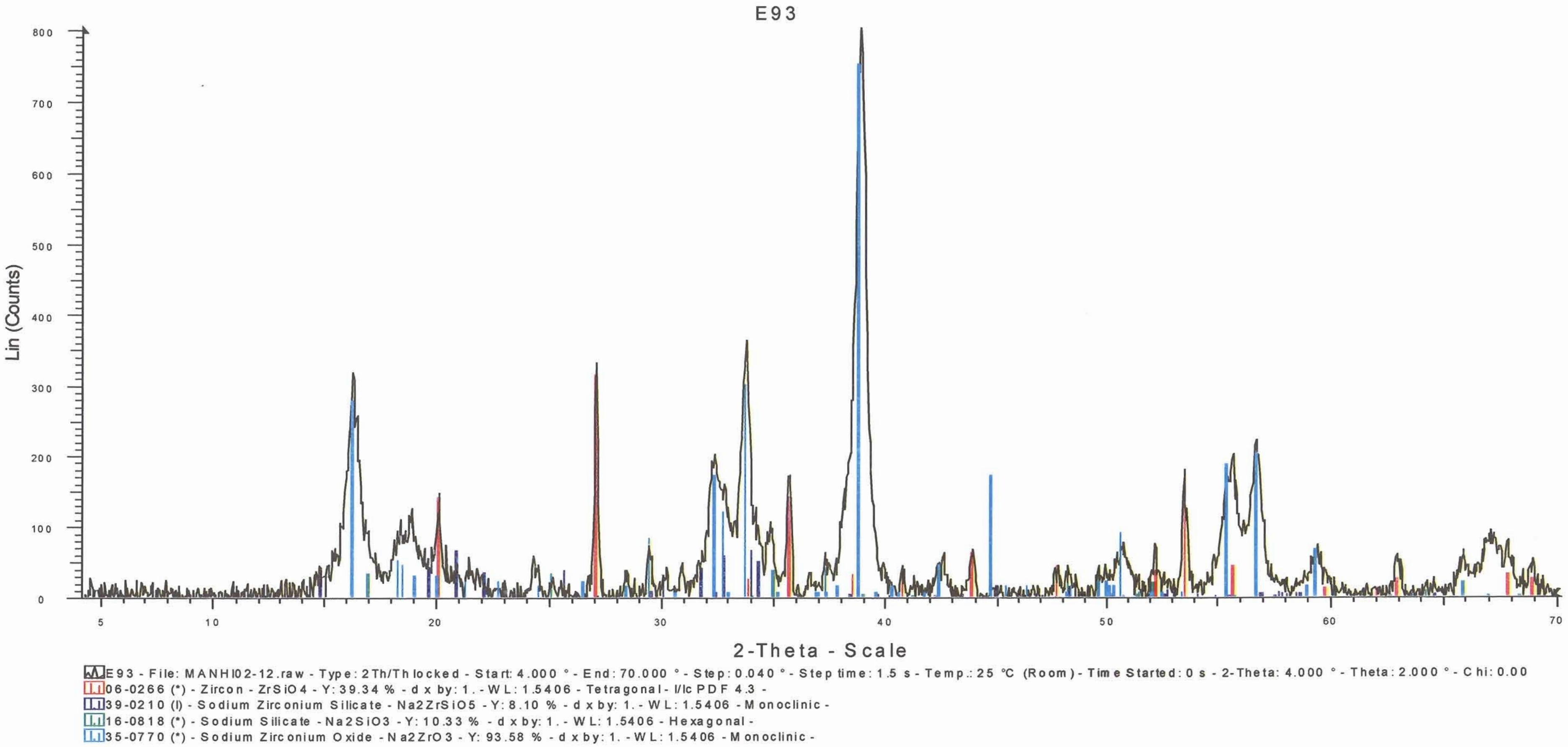


Spectrum 20: XRD spectrum of zircon alkali fused. A mole of zircon d ≈ 9.0 μm was fused with four moles of sodium hydroxide at 850ºC for two hours with intermediate milling at one hour.



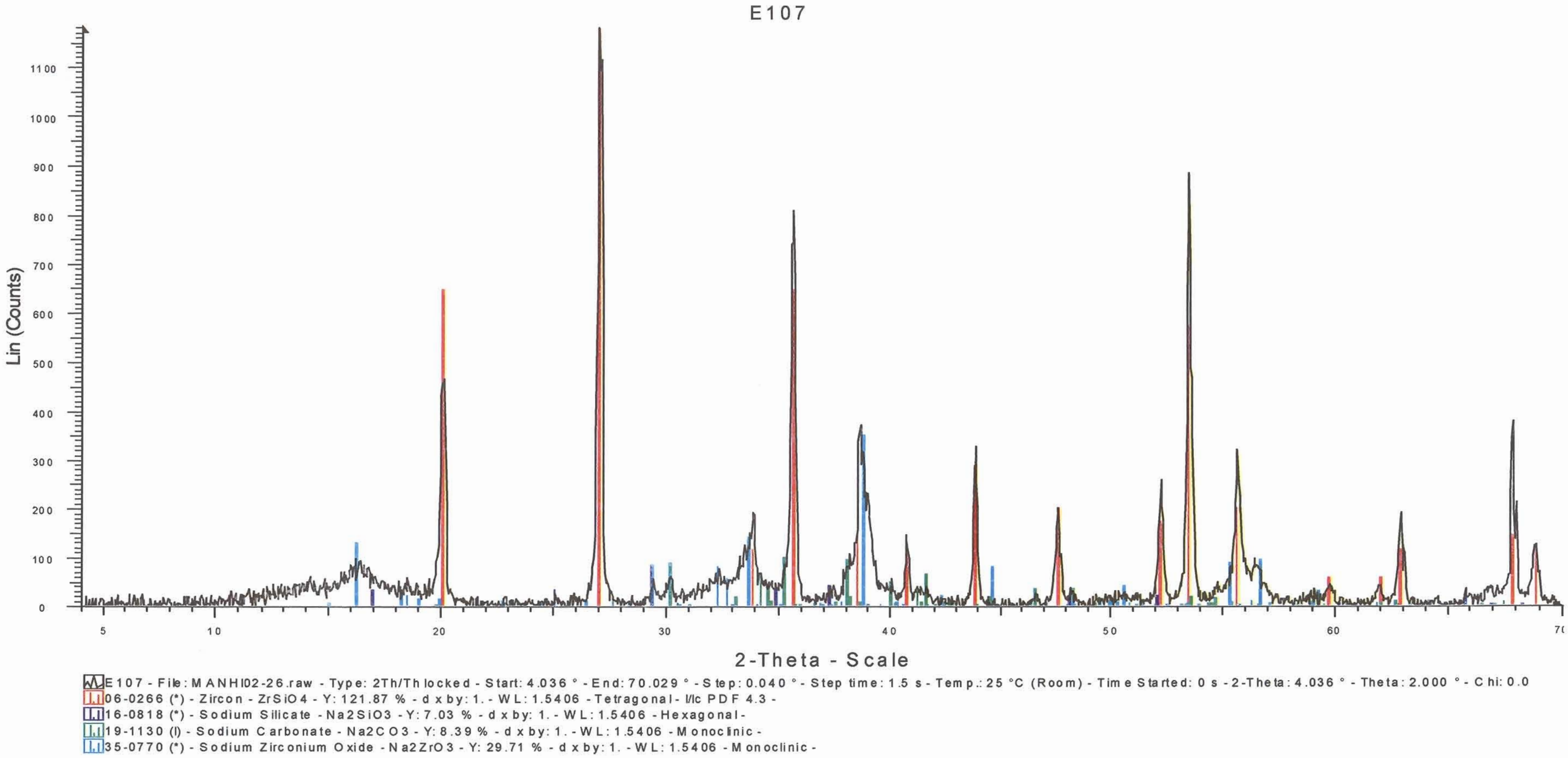
Spectrum 21: XRD spectrum of zircon alkali fused. A mole of zircon d ≈ 9.0 µm was fused with two moles of sodium hydroxide at 850°C for 2 hours with intermediate milling.

Appendix A

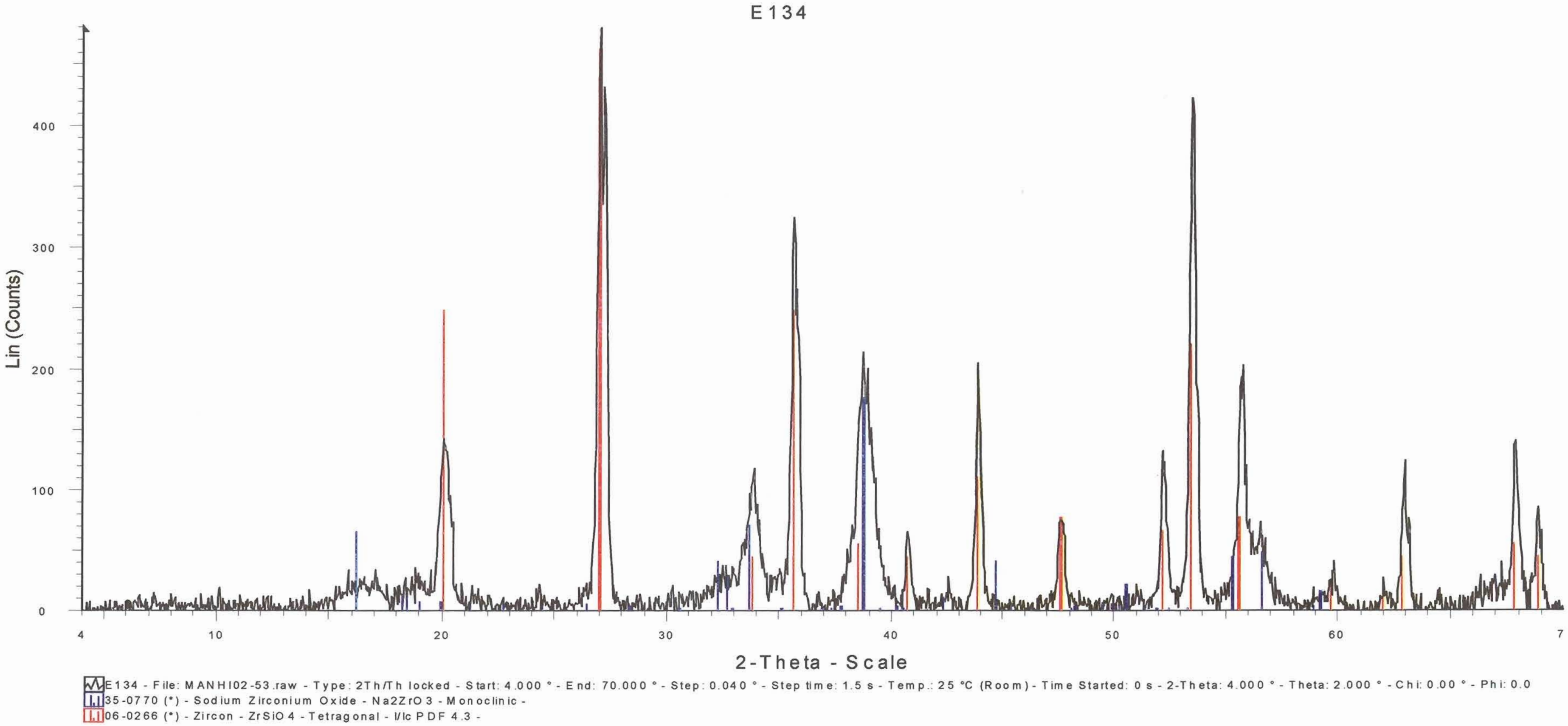


Spectrum 22: XRD spectrum of zircon alkali fused. A mole of zircon d ≈ 9.0 μm was fused with four moles of sodium hydroxide at 850°C for two hours with intermediate milling.

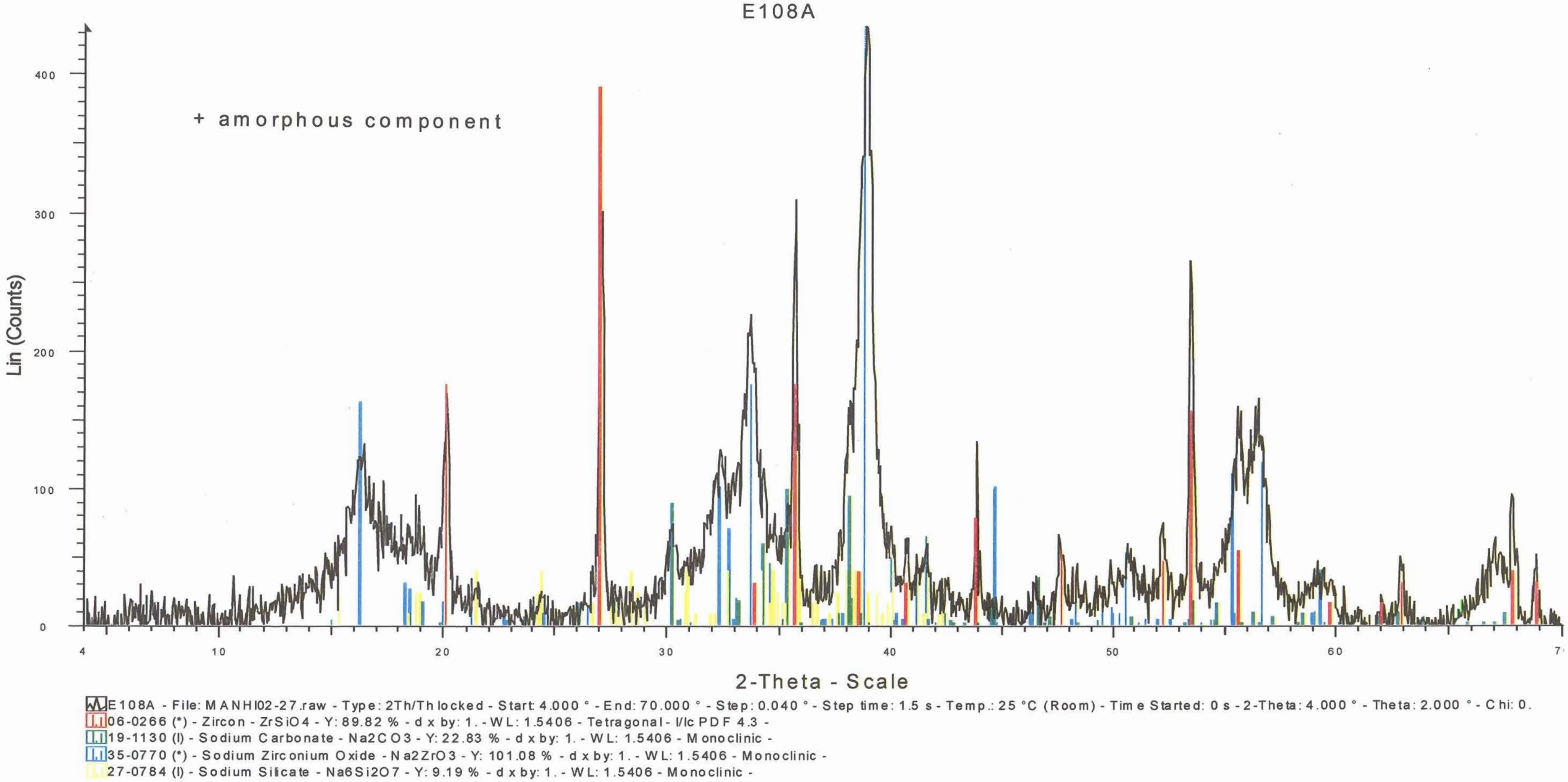
]



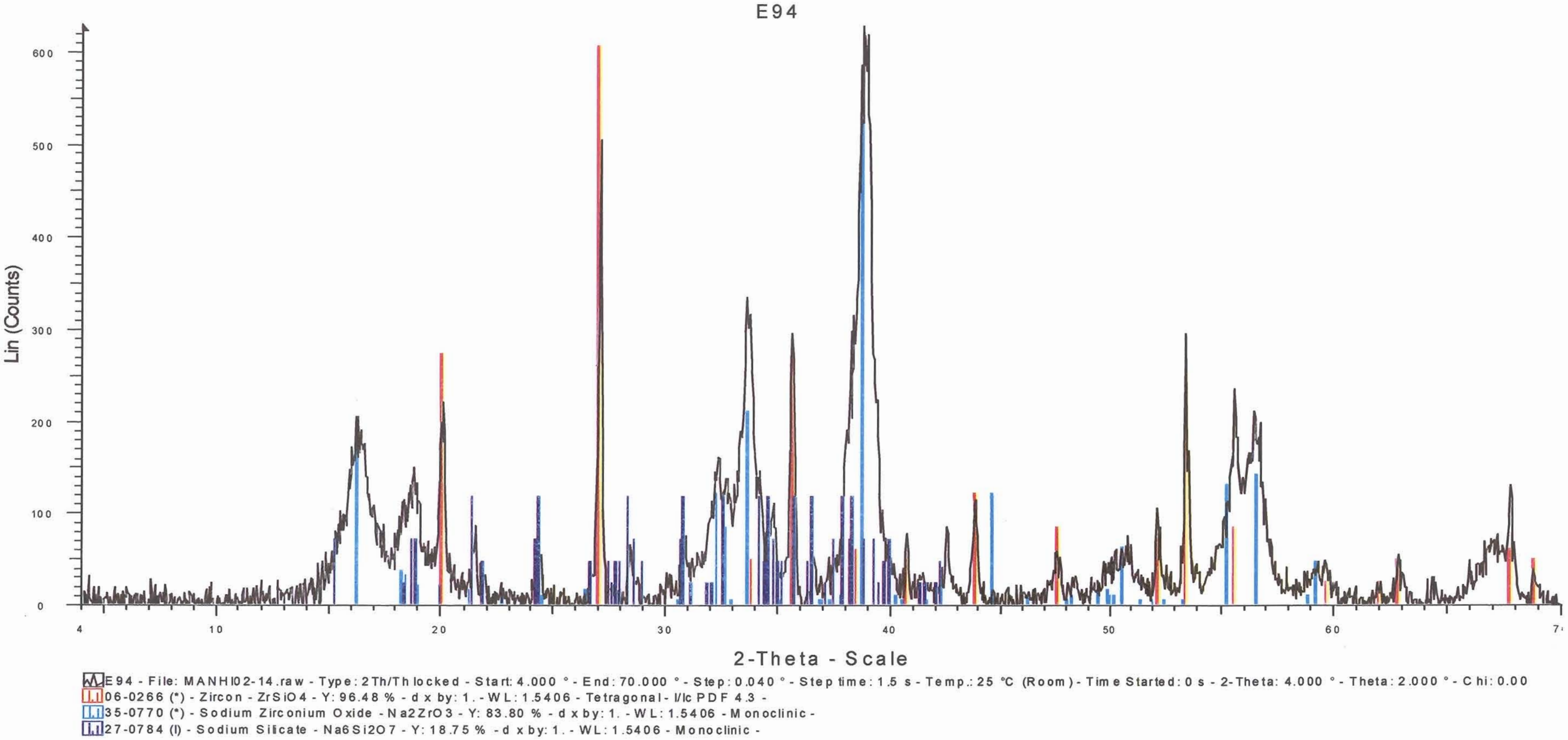
Spectrum 23: XRD spectrum of zircon alkali fused. A mole of zircon d ≈ 9.0 µm was fused with two moles of sodium hydroxide at 650°C for two hours with intermediate milling.



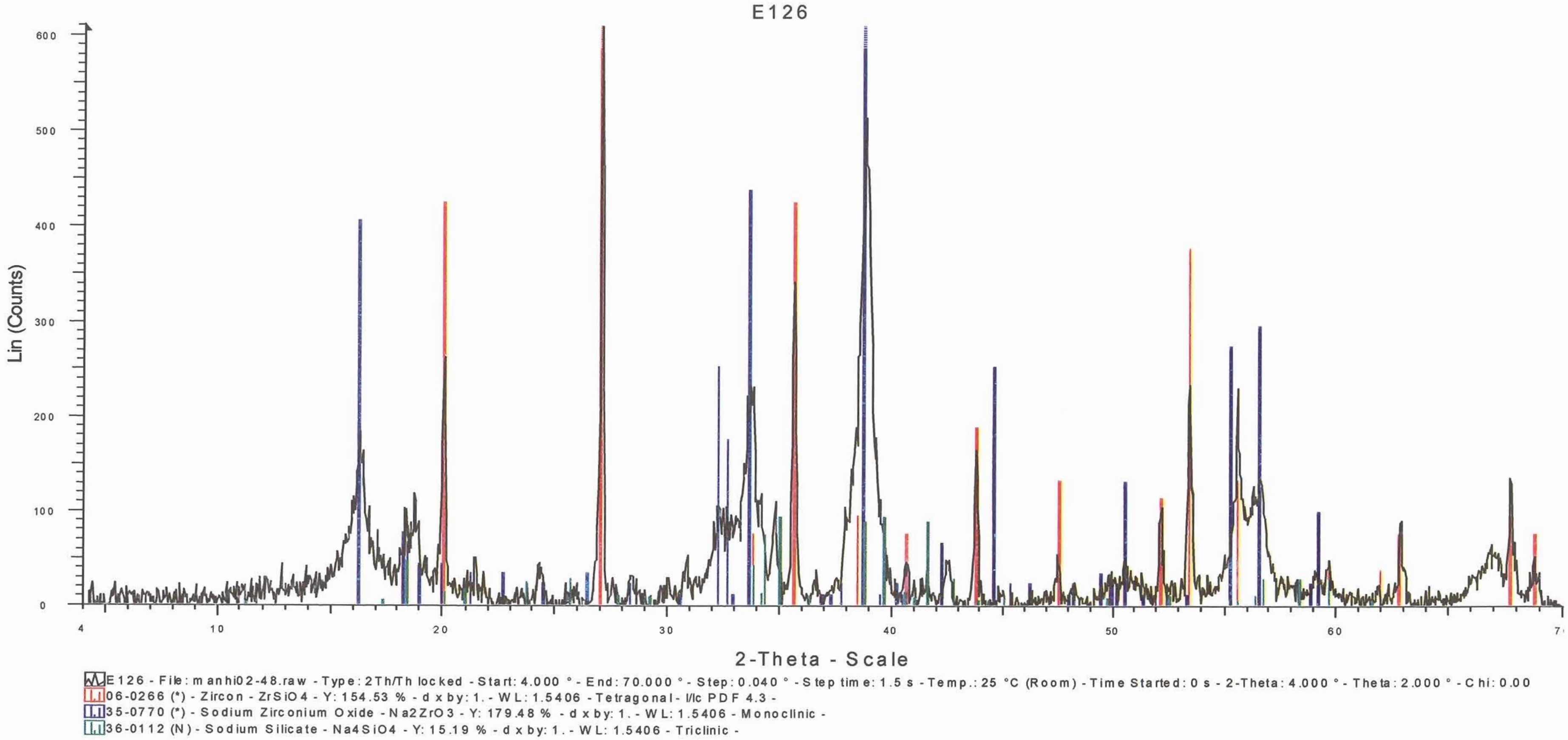
Spectrum 24: XRD spectrum of zircon alkali fused. A mole of zircon d ≈ 9.0 µm was fused with two moles of sodium hydroxide at 650°C for four hours with intermediate milling



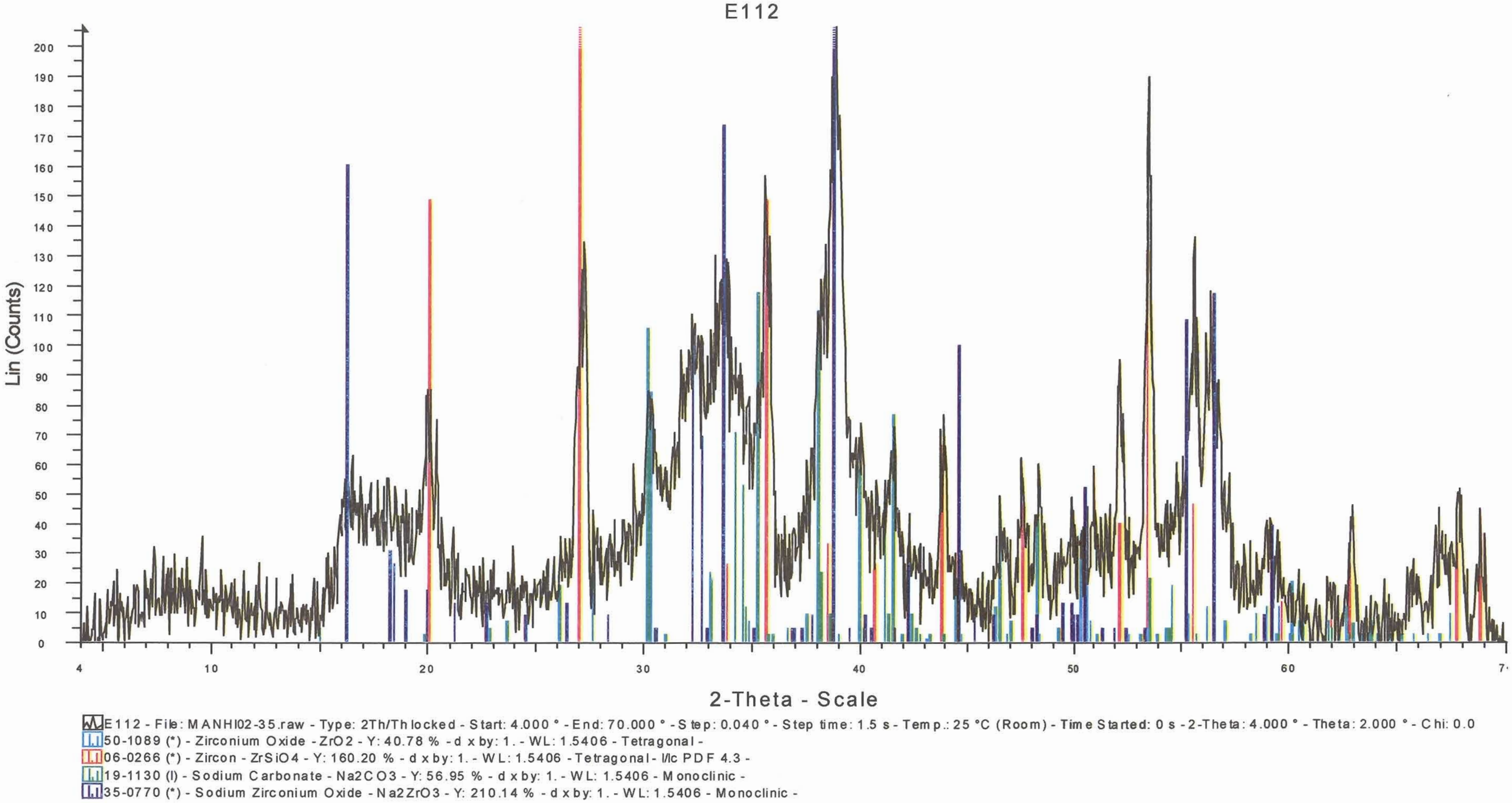
Spectrum 25: XRD spectrum of zircon alkali fused. A mole of zircon d ≈ 9.0 μm was fused with four moles of sodium hydroxide at 650°C for one hour with intermediate milling.



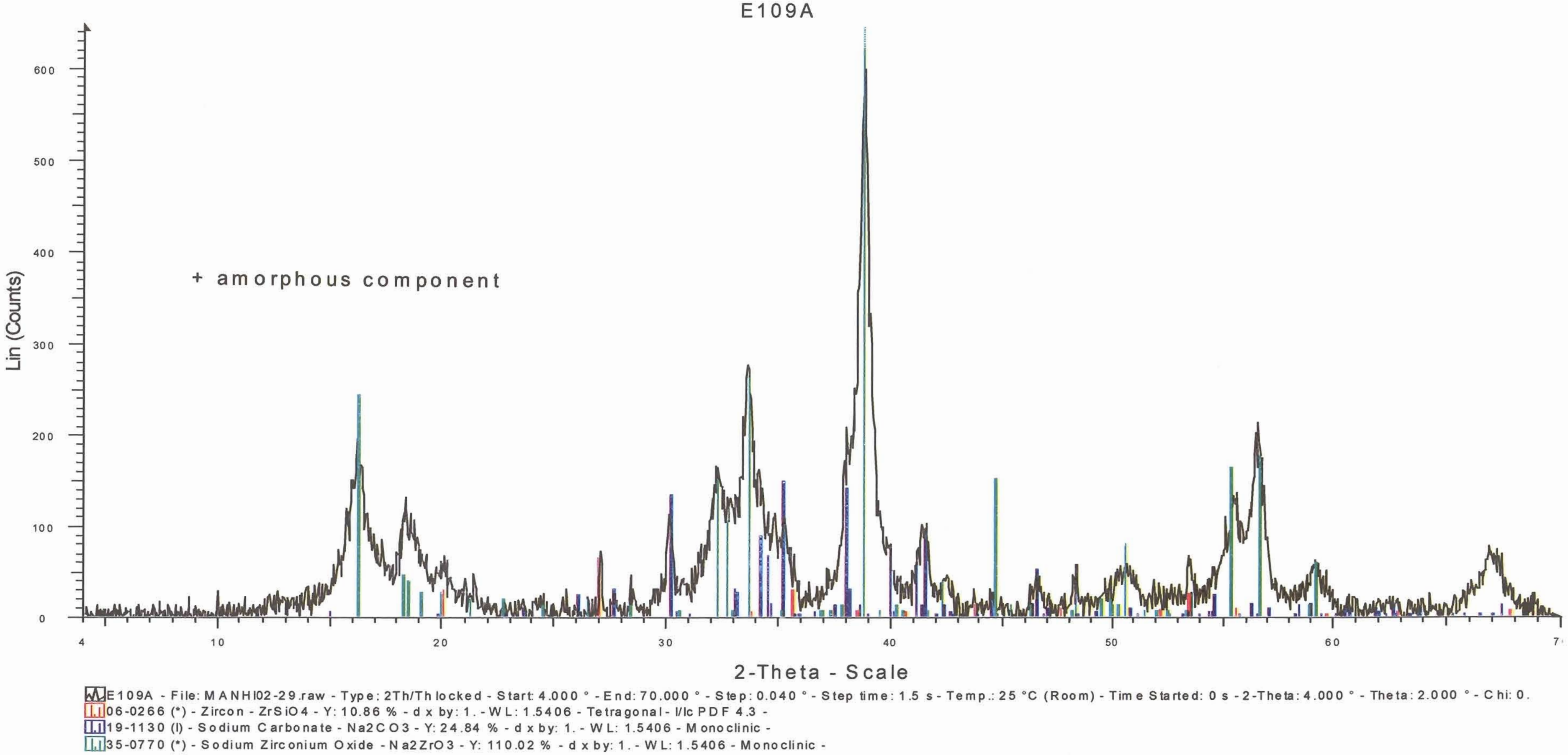
Spectrum 26: XRD spectrum of zircon alkali fused. A mole of zircon d ≈ 9.0 μm was fused with four moles of sodium hydroxide at 650°C for two hours with intermediate milling.



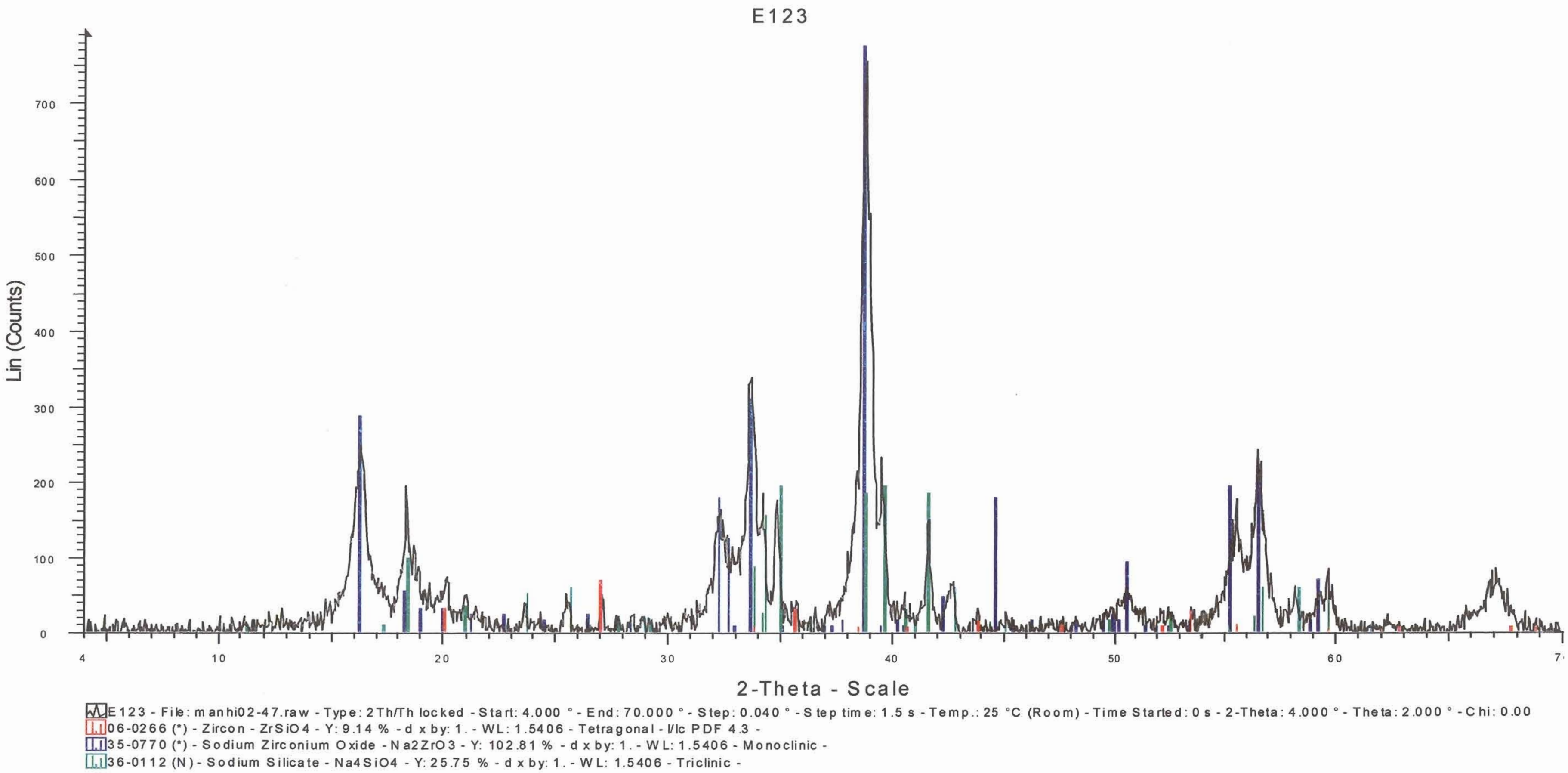
Spectrum 27: XRD spectrum of zircon alkali fused. A mole of zircon d ≈ 9.0 μm was fused with four moles of sodium hydroxide at 650°C for four hours with intermediate milling.



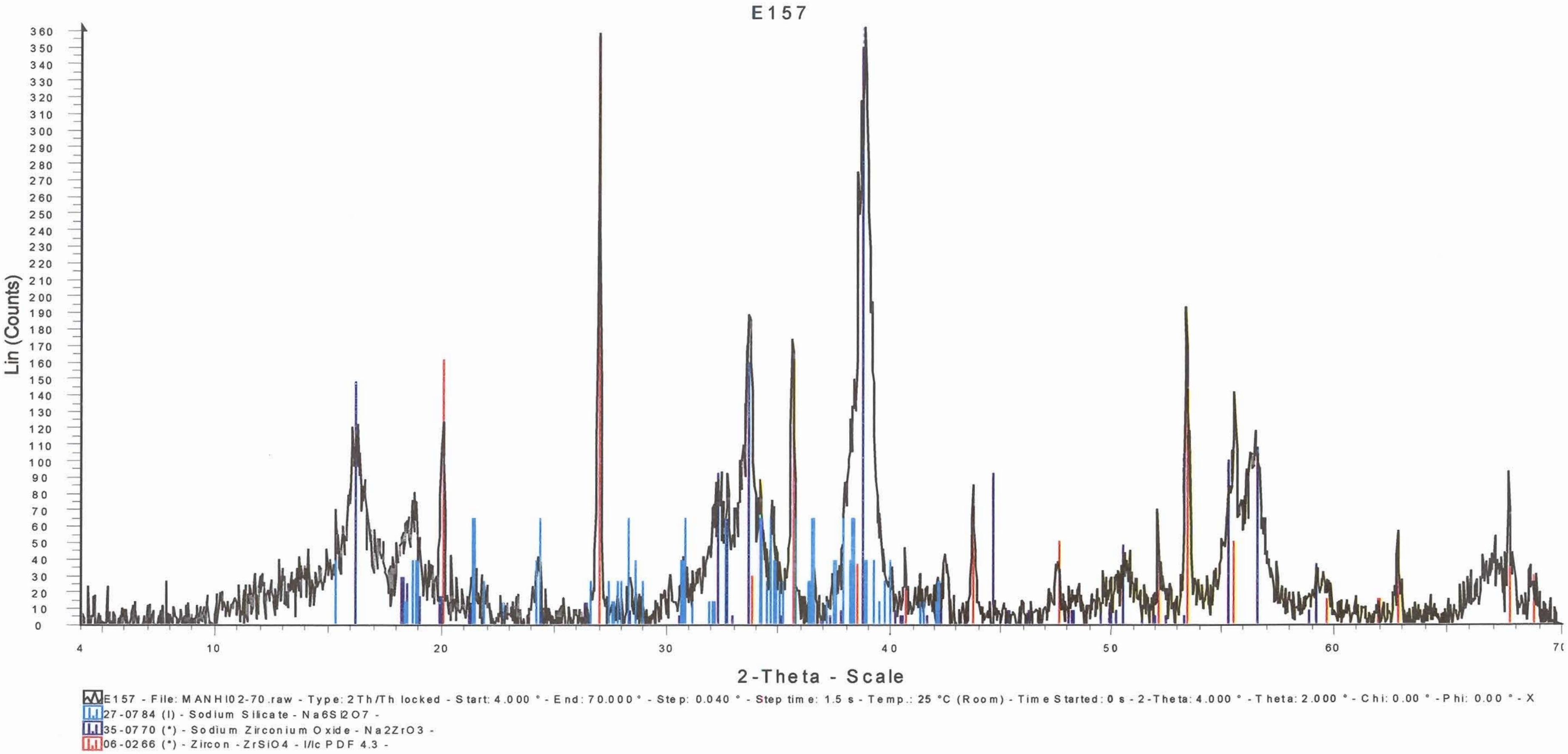
Spectrum 28: XRD spectrum of zircon alkali fused. A mole of zircon d ≈ 9.0 μm was fused with four moles of sodium hydroxide at 650°C for 24 hours with intermediate milling.



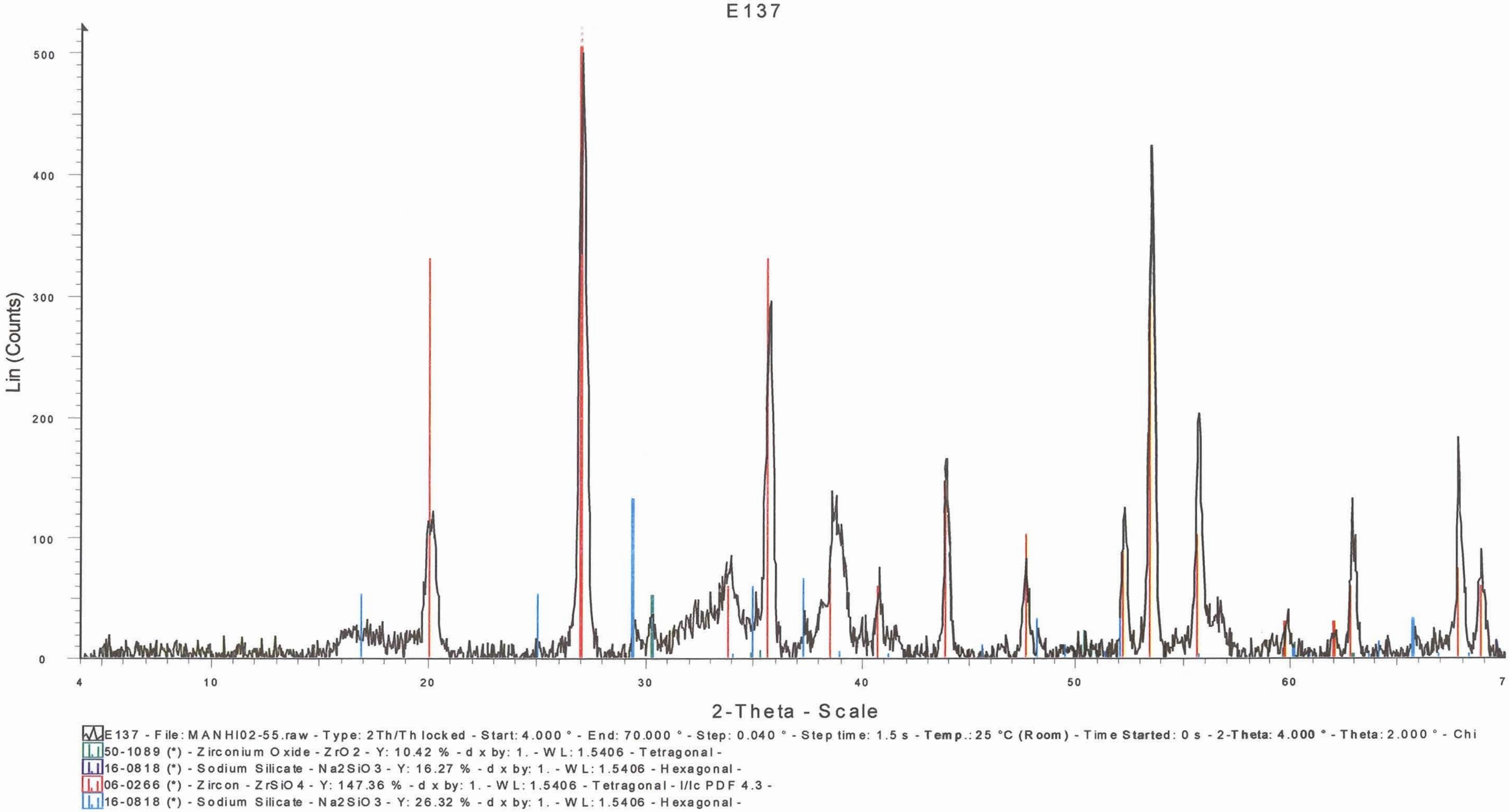
Spectrum 29: XRD spectrum of zircon alkali fused. A mole of zircon d ≈ 9.0 μm was fused with six moles of sodium hydroxide at 650°C for one hour with intermediate milling.



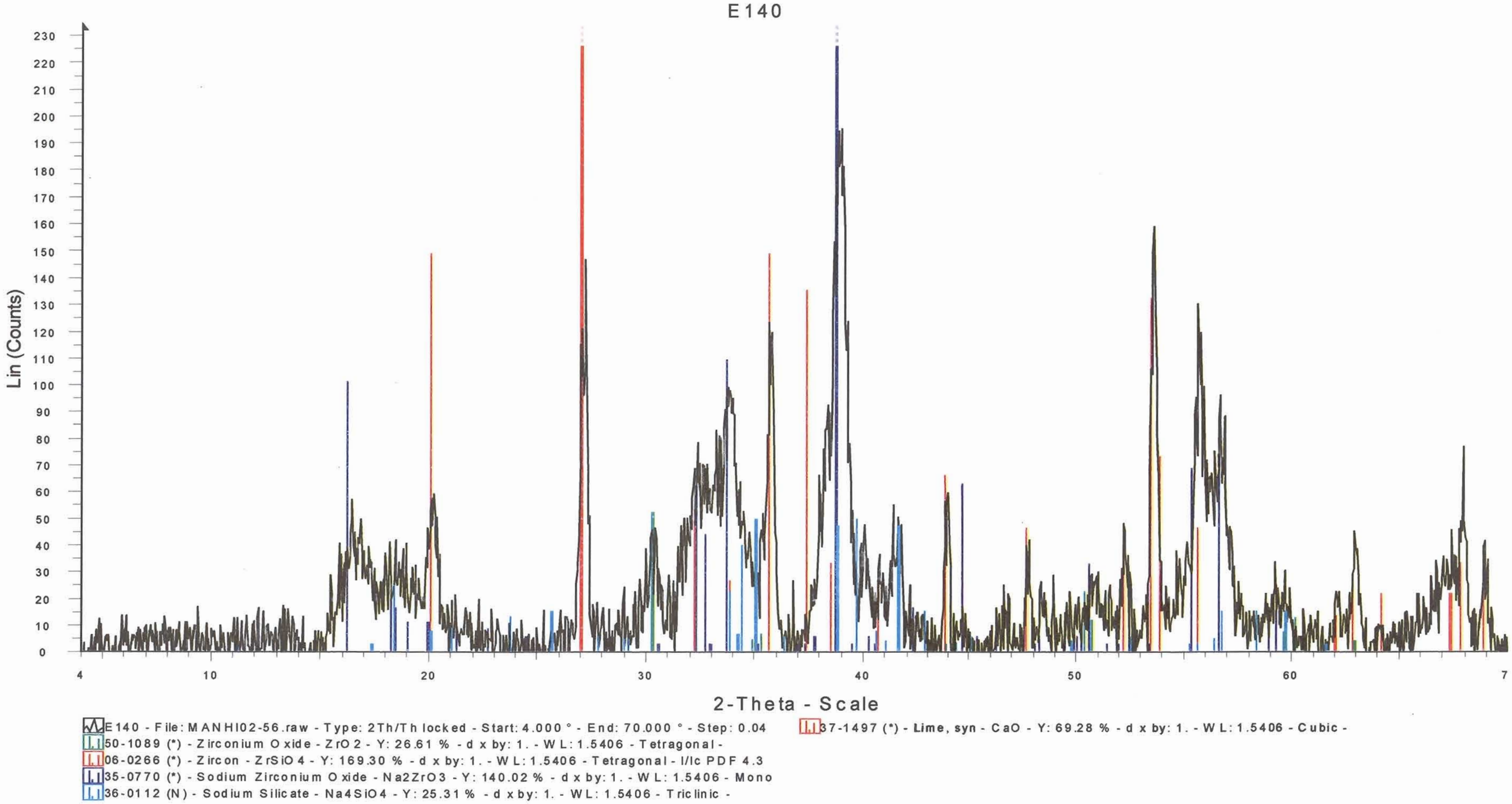
Spectrum 30: XRD spectrum of zircon alkali fused. A mole of zircon d ≈ 9.0 μm was fused with six moles of sodium hydroxide at 650°C for two hours with intermediate milling.



Spectrum 31: XRD spectrum of zircon alkali fused. A mole of zircon d ≈ 9.0 µm was fused with four moles of sodium hydroxide at 700°C for four hours with intermediate milling.



Spectrum 32: XRD spectrum of zircon alkali fused. A mole of zircon d ≈ 9.0 μm was fused with two moles of sodium hydroxide at 750°C for two hours with intermediate milling.



Spectrum 33: XRD spectrum of zircon alkali fused. A mole of zircon d ≈ 9.0 μm was fused with four moles of sodium hydroxide at 750°C for two hours with intermediate milling.

Appendix B

Table of values obtained in 336 hours decomposition.

Temperature	NaOH:$ZrSiO_4$	$ZrSiO_4$	NaOH	ZrO_2	Silica	NaOH in solids	NaOH in liquids
(°C)	(mols)	(g used)	(g used)	(% recovered)	(% recovered)	(%)	(%)
600	2:1	36,60	16,15	42,77	0	30,07	69,93
650	2:1	36,75	16,33	42,60	35,89	32,91	67,09
700	2:1	36,66	16,34	50,01	29,24	40,06	59,94
750	2:1	36,65	16,08	55,51	20,53	45,43	54,57
850	2:1	36,61	16,35	90,47	0	96,28	3,72
850	4:1	36,68	32,63	23,83	6,77	43,17	56,83

°C – temperature in degrees Celsius;

g – mass in grams;

% - Percentage in mass basis

Appendix C

Table of values obtained on fusion at 850 °C using two mols of sodium hydroxide per mol of zircon.

Time	NaOH:$ZrSiO_4$	$ZrSiO_4$	NaOH	ZrO_2	Silica	NaOH in solids	NaOH in liquids
(h)	(mols)	(g used)	(g used)	(% recovered)	(% recovered)	(%)	(%)
1	2:1	36,65	16,36	44,06	22,88	27,47	72,52
2	2:1	36,62	16,37	63,87	19,68	32,91	67,09
4	2:1	36.62	16.29	49,38	27,64	24,73	75,23
24	2:1	36,62	16,25	59,88	29,26	43,89	56,11
336	2:1	36,60	16,39	91,84	0	3,72	96,28

°C – temperature in degrees Celsius;

g – mass in grams;

% - Percentage in mass basis

Appendix D

Table of values obtained on fusion at 750°C.

Time	NaOH:$ZrSiO_4$	$ZrSiO_4$	NaOH	ZrO_2	Silica	NaOH in solids	NaOH in liquids
(h)	(mols)	(g used)	(g used)	(% recovered)	(% recovered)	(%)	(%)
2	2:1	36,62	16,33	38,63	35,49	9,48	90,52
4	2:1	36,63	16,29	38,49	23,63	10,68	89,32
336	2:1	36,60	16,15	54,94	19,11	32,91	67,09
2	4:1	36,61	32,28	62,02	64,41	13,61	86,39
4	4:1	36,63	32,33	73,04	44,31	8,8	91,20

°C – temperature in degrees Celsius;

g – mass in grams;

% - Percentage in mass basis

Appendix E

Table of values of relative mass in the decomposed product.

Time (h)	Na_2ZrO_3	Na_2ZrSiO_5	$ZrSiO_4$
1	0.26	0.23	0.51
2	0.21	0.41	0.39
4	0.30	0.19	0.50
24	0.31	0.30	0.40
336	0.03	0.87	0.10

Appendix F

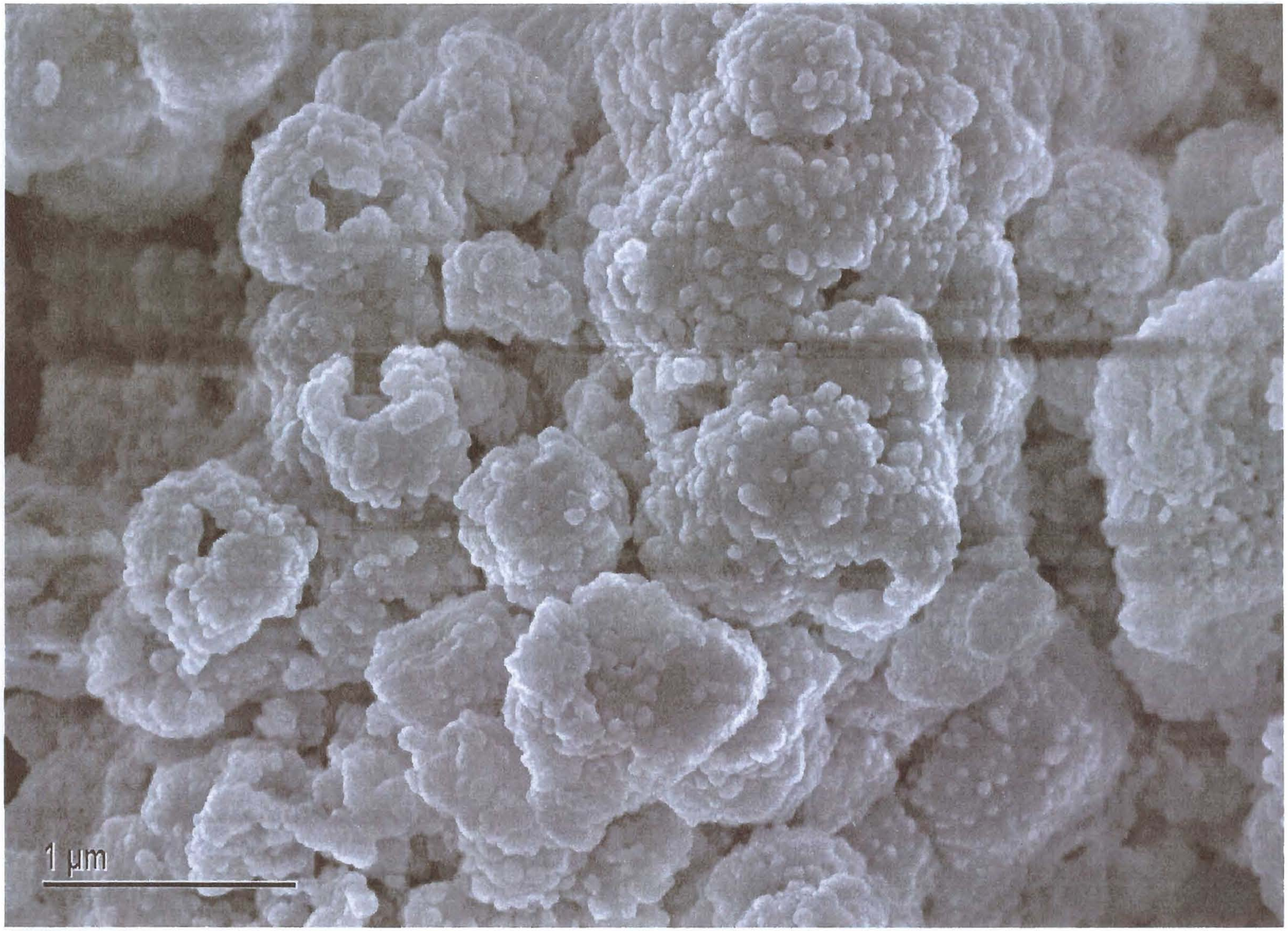
Table of values obtained on fusion of a mol of zircon with four mols of sodium hydroxide at 850 °C (direct synthesis).

Time	Temperature	$ZrSiO_4$	NaOH	ZrO_2	Silica	NaOH in solids	NaOH in liquids
(h)	(°C)	(g used)	(g used)	(% recovered)	(% recovered)	(%)	(%)
4	850	36,61	32,39	69,77	61,34	6,35	93,65
8	850	36,62	32,47	79,43	59,47	7,69	92,31

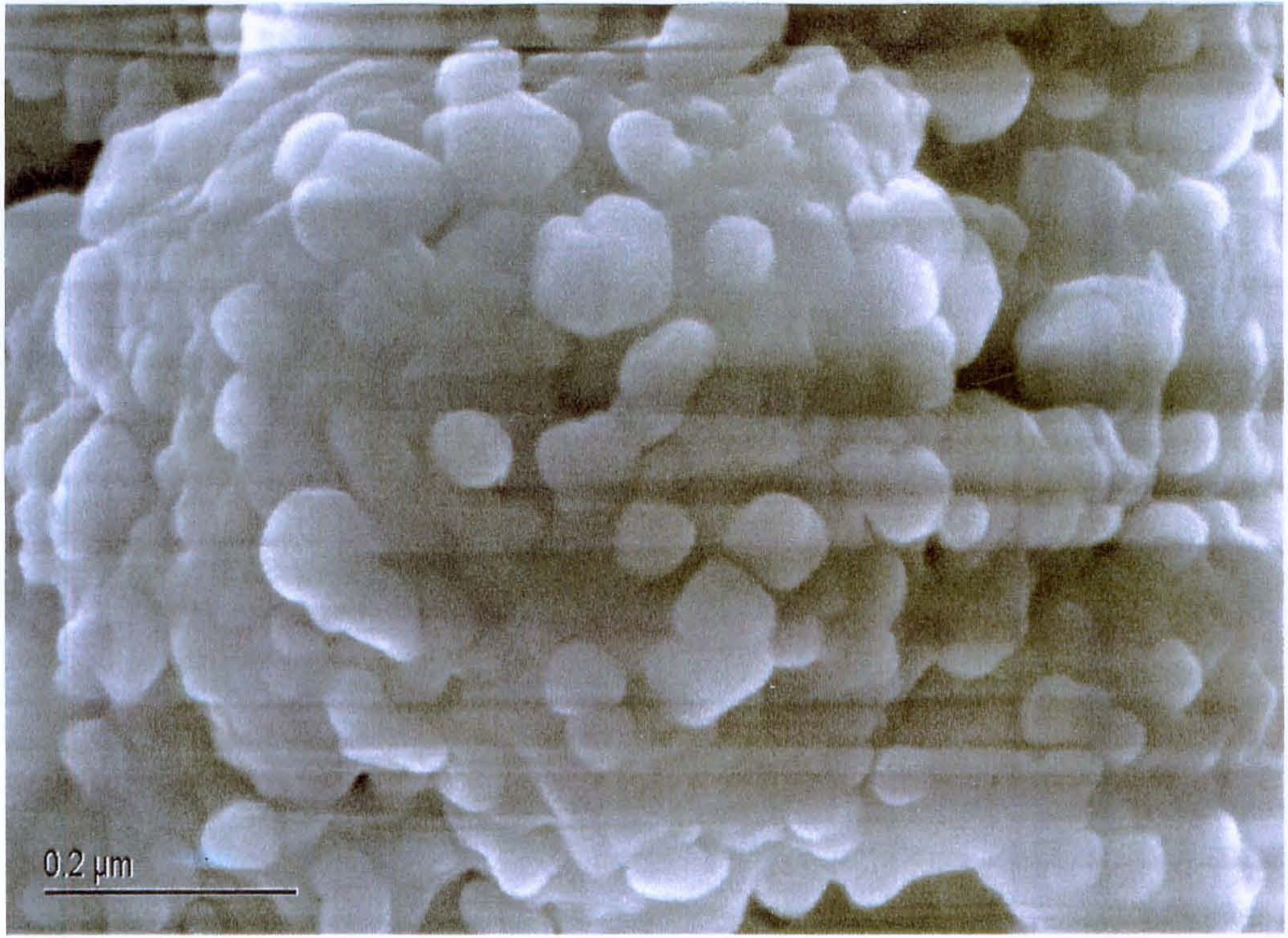
°C – temperature in degrees Celsius;

g – mass in grams;

% - Percentage in mass basis



Appendix G
Microphotograph of zirconia produced by direct route



Appendix G
Microphotograph of zirconia produced by direct route