

# **Raman signatures of the modern pigment (Zn,Cd) $S_{1-x}Se_x$ and glass matrix of a red bead from Magoro Hil, an archaeological site in Limpopo Province, South Africa, recalibrate the settlement chronology**

Linda C. Prinsloo\*, Jan C.A. Boeyens#, Maria M. van der Ryst# and Geoffrey Webb\*

\*Department of Physics, University of Pretoria, Pretoria, South Africa, 0002

#Department of Anthropology and Archaeology, University of South Africa, Pretoria, South Africa, 0003

## **Abstract**

Two glass trade beads, one red and one yellow, retrieved from a secure archaeological context on Magoro Hill, an erstwhile Venda stronghold in South Africa's Limpopo Province, were analyzed with Raman and photoluminescence spectroscopy. Raman spectroscopy identified the pigment coloring the yellow bead as lead tin yellow Type II and the glass as a typical soda-lime-silica glass. Both pigments and glass type were in use over a long time span and therefore the bead cannot be used as a temporal marker. The pigment coloring the red bead, on the other hand, was identified as nano-(Zn,Cd) $S_xSe_{x-1}$  mixed crystals, a pigment that was only widely used in the early 20<sup>th</sup> century. This date casts doubt on local oral tradition that associates the brick-built structure from which the beads were recovered with Manzinzinzi, a Venda chief who, according to contemporary documentary accounts, had already passed away in the 1880s. The more recent date for the red bead resolves the apparent discord between the oral and written records, suggesting that the building was probably erected and/or occupied by one of Manzinzinzi's successors.

## **Key-words**

Raman Spectroscopy, semiconductor, photoluminescence, archaeology, cadmium sulfoselenide, Magoro Hill

Corresponding author: Linda C Prinsloo  
Department of Physics  
University of Pretoria  
Pretoria  
South Africa  
27 12 420 2458  
linda.prinsloo@up.ac.za

## **1. Introduction**

Recently it was illustrated that Raman spectroscopy is a very useful method to study glass trade beads as information about the glass structure, as well as the pigments used to color the glass, is encapsulated in one spectrum.<sup>1-3</sup> Identification of the pigments used to color the beads can also be used to broadly date a specific bead if, as in the case of synthetic pigments, the first manufacturing date is known. In southern Africa glass trade beads are found at many archaeological sites of the past two millennia and testify to international trade. Information about the origin of the beads and their date of production can in many instances help in the historical reconstruction of a site's occupation.<sup>1-3</sup>

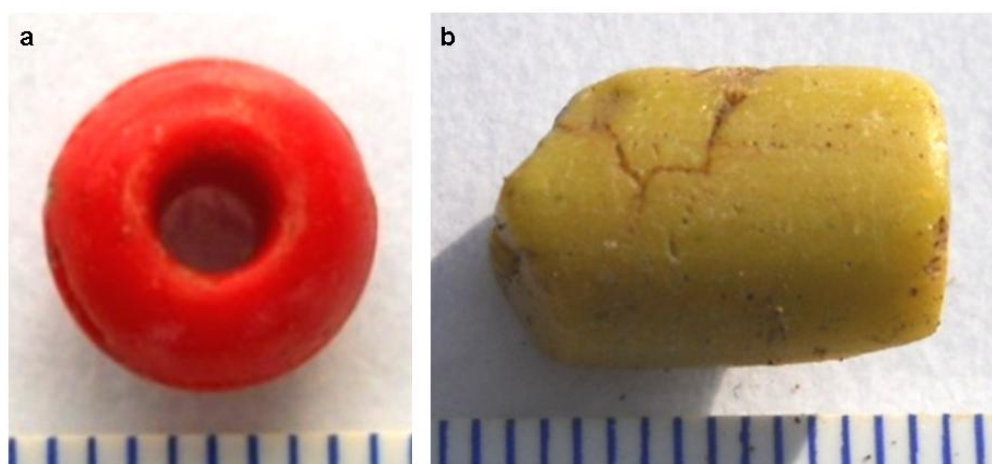
In sub-Saharan Africa this is very important as only a very few written records exist of the pre-Portuguese era and records thereafter often tend to privilege the history of European colonists in their interaction with Africans. The documentary record on African societies remains shallow even late into the 19<sup>th</sup> century, which implies that oral tradition and archaeology are often the main sources of information on underrepresented or marginalized groups. Oral chronologies are fickle, though, since traditions can be affected by memory loss, feedback, selection, reinterpretation, lengthening and telescoping. Fortunately they can be verified in some instances through physical archaeological evidence. In this regard, glass beads serve as useful temporal markers as long as their primary stratigraphic context is well established. Since they are small objects that can easily become lost or displaced, care should be taken to ensure that the matrix from which the beads are retrieved is truly associated with the occupational level that is to be dated. It should also be recognized that glass beads could have been treasured as heirlooms, and thus could pre-date an occupation.

## **2. The archaeological context**

Current historical archaeological research at Magoro Hill (nearest town Louis Trichardt), an erstwhile Venda stronghold in South Africa's Limpopo Province, aims to unravel the site's complicated settlement sequence. The Magoro Hill complex was located on the fringes of colonial settlement and seldom visited by literate observers

during the 19<sup>th</sup> century. Extant oral traditions relate that at least four chiefs reigned from the stronghold during this period of time<sup>4</sup> and that each successive chief occupied a separate residential unit on the eastern side of the hill. The foundations of a brick-built structure, attributed by the current leader of the Magoro community to the residence of Manzinzi, who is remembered and revered as a forceful chief and renowned traditional healer, formed part of the excavations. The rectilinear structure could be confidently dated to the colonial contact period as Venda houses traditionally consisted of dome-on-cylinder huts, the walls of which were constructed of wattle and daub, covered by a thatched grass roof. Contemporary documentary sources testify that Manzinzi passed away sometime during the 1880s.<sup>5</sup>

There are no contemporary documented descriptions or exact locations of the residences of either Manzinzi or his successors. The excavated material cultural remains therefore have to serve as an independent test of Magoro Hill's oral geography and the chieftom's dynastic chronology. Excavations of the brick-lined foundations of the structure exposed two compartments. The bright red bead (Fig. 1a), one of three such pigmented beads, was recovered in primary context inside the collapsed smaller compartment of the building, which probably served as a bedroom.



**Figure 1: The beads from Magoro Hill investigated in this study a) one of three bright red beads and c) large yellow bead which appears heavily corroded.**

Similarly the yellow bead (Fig.1b), which was unearthed from the larger compartment, was found in a sealed context on the original floor level of the building, about 10 cm below the present surface layer. The provenance of the two analyzed beads is therefore secure and their association with the excavated structure beyond doubt.

A preliminary visual inspection of the excavated beads drew attention to the molded bright red beads and their possible resemblance to the selenium-colored beads depicted in Francis.<sup>6</sup> Since Francis proffers a post-1890 date for the introduction of selenium in bead-making, a date that does not correspond with Manzinzi's period of rule, it was decided to spectroscopically analyze one of the red beads as well as the conspicuously large yellow bead.

## **2. Samples**

The two beads analyzed can be seen in Figure 1. The first is a bright red (Fig. 1a), barrel-shaped bead, in pristine condition and manufactured by using a mold. The second is a bright yellow hand-drawn cylinder (Fig. 1b), which appears quite weathered.

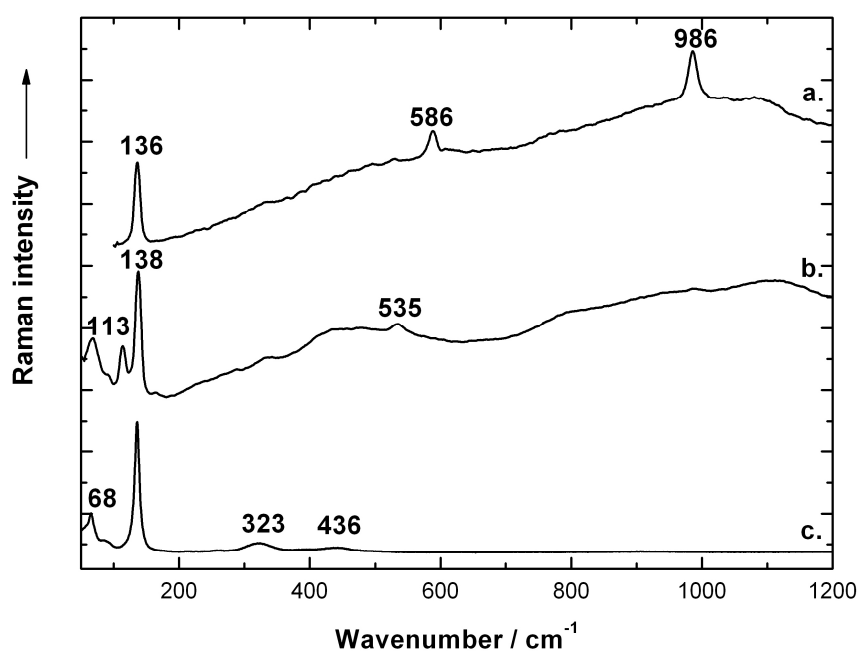
## **3. Experimental detail**

The Raman and room temperature photoluminescence spectra were recorded with a T64000 micro-Raman spectrometer from HORIBA Scientific, Jobin Yvon Technology (Villeneuve d'Ascq, France). The Raman spectra were excited with either the 514.5 or 488 nm lines of a Coherent Innova<sup>®</sup> 70C Series Ion Laser System and the 100x or 50x objectives of an Olympus microscope was used to focus the laser beam (spot size ~ 2-12  $\mu\text{m}$ ) on the samples and also collected the backscattered Raman signal. An integrated triple spectrometer was used in the double subtractive mode to reject Rayleigh scattering and dispersed the light onto a liquid nitrogen-cooled Symphony CCD detector. The spectrometer was calibrated with the silicon phonon mode at  $520.6\text{ cm}^{-1}$ .

## 4. Results and discussion

### 4.1 Pigments coloring the beads

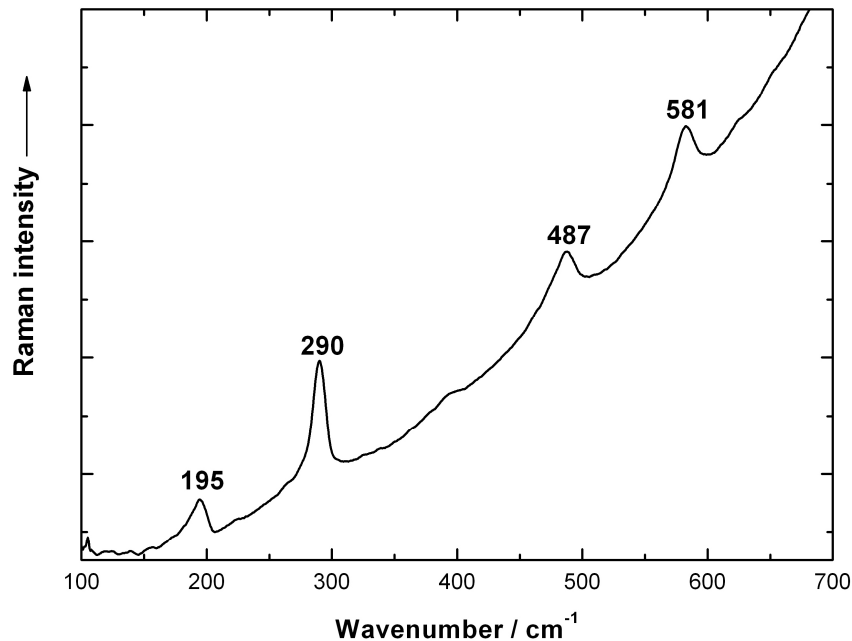
Glass coloring is usually obtained by doping the glass with  $3d/4f$  ions or dispersing colored crystalline phases (pigments or metal nanoparticles) in the glass matrix.<sup>7</sup> Coloring obtained by doping disperses ions (e.g. Co) throughout the silicate matrix and in many instances no special Raman signal can be observed.<sup>7</sup> Small crystallites of a pigment are sometimes distinguishable under a microscope objective (especially in ancient glasses), which makes it possible to focus on the pigment directly and obtain a spectrum that can be identified by comparing it with a spectral library of reference material. Since the first publication of a spectral library (56 inorganic pigments used before 1850), various other libraries have been compiled and are readily available through the internet.<sup>8</sup>



**Figure 2: Raman spectra recorded on the yellow bead of the pigment coloring the yellow glass and other crystalline phases.**

Raman spectra recorded on the pigment coloring the yellow bead are given in Figure 2 (a-c) and can either belong to Naples yellow ( $\text{Pb}_3(\text{SbO}_4)_2$ ) with Raman bands at 140 (vs), 329 (m, br) and 448 (w, br) or lead tin yellow type II ( $\text{PbSn}_{1-x}\text{Si}_x\text{O}_3$ ) with bands at 138 (vs), 324 (m, br).<sup>9</sup> The spectral profile of the two pigments is very similar (both have a pyrochlore structure) and it is therefore difficult to distinguish between them based on their Raman spectra only. Furthermore Naples yellow forms large solid

solutions with almost any metal such as Sn, Zn and Fe and the type of metal ion shifts the main peak between 122-141  $\text{cm}^{-1}$  and therefore identifying the exact solid solution is not clear-cut.<sup>10</sup> However, comparing the wavenumber positions of the peaks in the spectrum of the large yellow bead to Table 3 of reference 10, where the wavenumber positions of a large number of Raman spectra of Pb-Sn-Sb solid solutions are listed (together with composition), it most closely resembles that of lead tin yellow Type II. It is also an exact match of the spectra of lead tin yellow Type II reported in references 3 & 11 (both position and relative intensity of bands). It is therefore highly likely that the pigment coloring the yellow bead is lead tin yellow Type II. Spectrum 3c was recorded on a large yellow crystal that was clearly visible under the microscope, which shows that the pigment was not finely ground before mixing into the glass and indicates an ancient manufacturing date, in line with the corroded appearance of the bead. In spectrum 2b two extra peaks 113  $\text{cm}^{-1}$  and 535  $\text{cm}^{-1}$  are also visible, attributed to red lead oxide that could have been added to enhance the color of the bead or could be a residue of the reagents used to produce the pigment. A similar spectrum was previously also observed in a small orange seed bead (Mapungubwe oblate) excavated on Mapungubwe Hill and Islamic ceramics from Dougga in Ifriqiya, one sample dating from the 11<sup>th</sup>-12<sup>th</sup> century (Zirides period), the other from the 17<sup>th</sup>-18<sup>th</sup> century (Ottoman period).<sup>1-3, 12</sup> Two other narrow bands (586, 986  $\text{cm}^{-1}$ ) are observed in spectrum 2a and probably originate from a pyroxene, which is characterized by a Si-O stretching mode above 800  $\text{cm}^{-1}$  and a Si-O bending mode between 500 and 760  $\text{cm}^{-1}$ . Pyroxene could have been present in the raw materials used and not completely dissolved into the glass matrix during the glassmaking process. In spectra a&b bands originating from the glass can also be observed. The pigment Naples yellow became popular in Italy during the Renaissance period but it was identified on tiles in Babylon from 16<sup>th</sup> c. BC.<sup>13-14</sup> Likewise lead-tin oxides have been employed since antiquity as yellow pigment and opacifiers,<sup>15</sup> but was replaced in Europe by Naples yellow as artists' pigment. According to its Raman spectrum the yellow pigment is lead tin yellow type II but the assignment is inconclusive without supportive elemental analyses. Both the two possible pigments have been in use since antiquity as opacifying and coloring agents in glass production and can therefore not provide information about the manufacturing date of the bead.

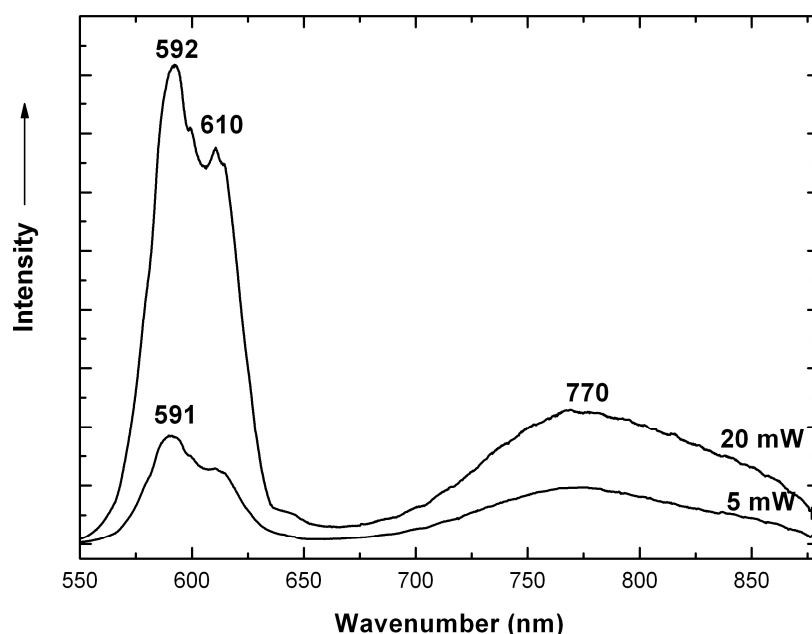


**Figure 3: Raman spectrum of the pigment coloring the red glass recorded with 514.6 nm excitation.**

In Figure 3 the Raman spectrum of the pigment coloring the red bead exhibits peaks at 195, 290, 487 and 581  $\text{cm}^{-1}$  and closely resembles a spectrum reported by Wang *et al.* for a mixture of Cd and Se  $\pm$  Zn.<sup>16</sup> An even closer resemblance is observed with a spectrum for antique glass published by Bouchard *et al.*<sup>17</sup> identifying the pigment as  $(\text{Zn,Cd})\text{S}_x\text{Se}_{x-1}$  nanocrystals dispersed within the glass matrix. The peaks at 195 and 290  $\text{cm}^{-1}$  can be attributed to LO-like phonons of the semi-conductors CdSe and CdS respectively. The peak positions show a hypsochromic shift in comparison to the LO phonons reported for the bulk materials which occur at 210 and 305  $\text{cm}^{-1}$  respectively<sup>18-19</sup> and the FWHM of both peaks have increased from  $\sim 5 \text{ cm}^{-1}$  for the bulk material to  $\sim 16 \text{ cm}^{-1}$ . Together with the asymmetric line shape of the peaks, these factors point to the fact that the crystals are nanosized with dimensions between 2-20 nm, causing the optical properties to differ from the bulk material.<sup>20-23</sup> Quantum confinement occurs when the dimensions of crystals are comparable or smaller than the exciton Bohr radius. The finite size of the clusters transforms the continuous band of the bulk crystal into a series of discrete states, or molecular-like orbitals, shifting the band gap to higher energies.<sup>21</sup> The other peaks in the spectrum are attributed to second-order peaks, visible due to a resonance enhancement with the 514.6 nm excitation laser line. The color hue of these pigments is determined by the amount of selenium added to the mixture (increasing selenium content red-shifting the color), as

well as the crystal sizes. The position and intensity of the LO-like peaks are dependent on the composition of the alloy and can therefore be used to determine the crystalline composition and, according to tables published in Bischof *et. al.*, this pigment consists of a proportion of 45% S or (S+Se).<sup>21</sup>

The spectrum in Figure 3 slopes upwards exponentially as it is superimposed on the luminescence band located at 596 nm (Fig. 4) associated with the band-edge emission from the  $\text{CdS}_x\text{Se}_{x-1}$  semi-conductor. Another luminescence band, attributed to deep traps far below the edge (red-shifted emission), occurs in the near infrared region of the spectrum and has been used to identify cadmium pigments in works of art as there are no other pigments with luminescence bands in this region.<sup>24</sup> In Figure 4 two spectra of the luminescence bands are presented, recorded with different laser powers. It is clear that in the spectrum recorded with the lower laser power the relative intensity of the bands differs. In-depth studies have been published of the resonance effects, linear and nonlinear effects and influence of laser power on the Raman and photoluminescence spectra of  $\text{CdS}_x\text{Se}_{x-1}$  nanoparticles in borosilicate glasses used as filters.<sup>20-23</sup> The Raman spectrum and typical luminescence spectrum of the pigment on the red bead identify it as  $\text{CdS}_x\text{Se}_{x-1}$  nanoparticles.



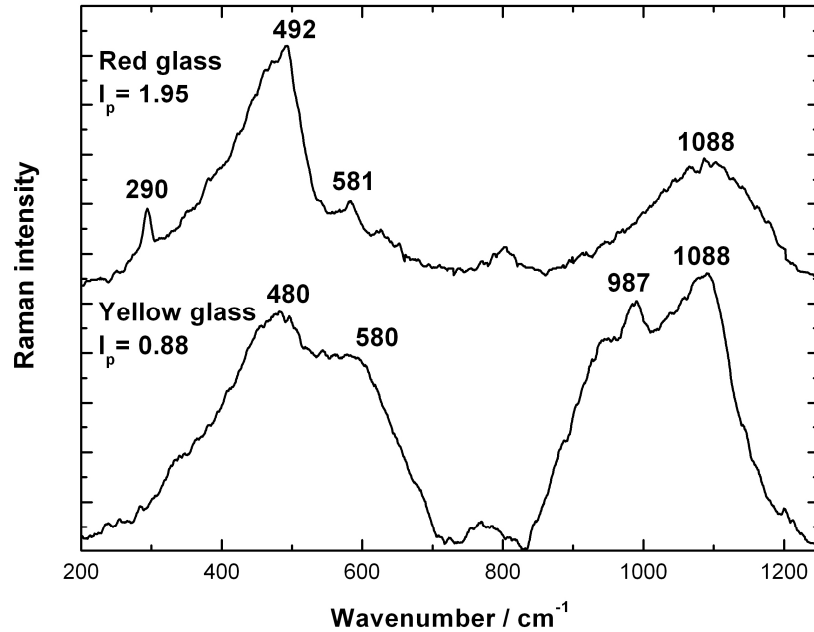
**Figure 4: Photoluminescence spectrum at room temperature of the red glass using 514.6 nm excitation using two different laser powers (mW and mW at the sample).**



Identifying the pigment as cadmium based is an interesting result in the light of the history of red Cd based pigments. In 1892 a German patent described cadmium sulfoselenide ( $\text{CdS}_x\text{Se}_{x-1}$ ) mixed crystals as a pigment for the first time and in 1910, as the element cadmium became more available, it was commercially sold as artists' pigment (cadmium red).<sup>24</sup> Because they were costly, expansion into a larger market awaited the development of co-precipitation with barium sulphate and zinc sulphide in the late 1920s, to create the more-economical cadmium lithopone pigments ( $\text{ZnS-CdSSe-BaSO}_4$ ).<sup>25</sup> It is probable that the use of this pigment to color mass-produced glass beads would have occurred at this time. In the 1990s, however, these pigments were being phased out in response to the public's concern about toxic cadmium in the environment.<sup>25</sup> This implies that the use of cadmium pigments on a large scale is limited to a small window of time, namely the 20<sup>th</sup> century. The identification of the pigment used to color the bead as  $\text{CdS}_x\text{Se}_{x-1}$  has implications for the dating of the site as the first commercial use of this pigment is the early 20<sup>th</sup> century, while the excavated house foundations are supposed to date from the 19<sup>th</sup> century.

#### *4.2 Raman spectra of the glass*

A glass is a dense alumina-silicate glassy phase doped or mixed with other metallic oxides, which act as flux to lower the firing temperature by breaking the Si-O linkages and decreasing the degree of polymerization in the Si-O network. In contrast to other analytical techniques which mostly identify crystalline phases present in a glass, Raman spectroscopy also provides information about the microstructure of the silicate network as it probes molecular bonds. The Raman spectrum of the amorphous phase of a glass consists of two broad bands around 500 and 1000  $\text{cm}^{-1}$ . The band around 500  $\text{cm}^{-1}$  originates from the  $\nu_2$  bending vibration of isolated  $\text{SiO}_4$  tetrahedra and the one around 1000  $\text{cm}^{-1}$  to coupled  $\nu_1$  and  $\nu_3$  Si-O stretching vibrations. In highly connected tetrahedral structures the bending modes have a high Raman intensity and in weakly connected tetrahedral units, as caused by the addition of fluxing (ionic) agents, the intensity of this band decreases and the stretching modes become more intense. The relationship between the Raman index of polymerization ( $I_p = A_{500}/A_{1000}$  with A being the area under the Raman band), the glass composition and the processing temperature is well documented.<sup>26-28</sup>



**Figure 5: Raman spectra of the red glass (488 nm excitation) and yellow glass (514.6 nm excitation).**

It was not possible to record the spectrum of the red glass matrix with the 514.5 nm laser line due to the overlap with the luminescence band and the 488 nm line was used. In Figure 5 the glass spectrum of the red bead is compared to that of the yellow bead (recorded with 514.6 nm excitation). The bending vibration is centered around 492  $\text{cm}^{-1}$  and the stretching vibration around 1088  $\text{cm}^{-1}$ , the two sharp peaks at 290 and 487 originate from the Raman spectrum of the pigment (see Fig. 3). In the spectrum of the glass of the red bead the bending vibration band has a much higher intensity than that of the stretching band and the polymerization index ( $I_p$ ) was calculated as  $I_p=1.95$ , which consigns the glass of the red bead to the same category of modern glass produced at a high firing temperature with a smaller percentage of fluxing agents.<sup>28</sup> This correlates well with the modern pigment identified as the coloring agent. It should be noted that not all modern glass has a high polymerization index, as for certain applications it is favorable to use a lower firing temperature by manipulating the amount of fluxing ions used.

In contrast, in the glass spectrum of the yellow bead the two bands are more or less of equal height with  $I_p = 0.88$ , which places it into the category of typical soda/lime glasses that have been manufactured since antiquity.<sup>28</sup> The peak at 987  $\text{cm}^{-1}$  is attributed to the  $\text{SO}_4^-$  stretching band of a sulphate and is typical of a glass melt that

has not been sufficiently annealed.<sup>290</sup> It has also been shown that a peak in this position together with the peak at  $480\text{ cm}^{-1}$  defines the glass as heavily corroded, which is more evidence that the yellow bead is older than the red one.<sup>30</sup>

#### *4.3 African glass trade beads*

Tens of thousands of glass beads have been recovered from archaeological sites in southern Africa dating from the 8<sup>th</sup> -16<sup>th</sup> century. On morphological characteristics, with supportive chemical analyses, Wood classified the beads into six distinct classes. The red bead does not fit into any of these classes and clearly originates from a later period.<sup>31</sup> According to Wood (personal communication, 2011) the yellow bead morphologically resembles beads excavated at Simunye in Swaziland, and several sites on the east coast of Africa, such as Sofala, Kilwa and the island Shanga, dating from the Portuguese occupation. The sites vary in age from the 12<sup>th</sup> century onwards to the 19<sup>th</sup> century.<sup>32</sup> Without further analyses of all the beads it is therefore not possible to put a date to the yellow bead. The pigments used and type of glass though indicate that the yellow bead probably was manufactured at an earlier date than the red bead and represents an heirloom. Old beads are still valued today in African societies and are often strung with recent beads as it is believed that the power associated with the older beads will be transferred to more modern specimens. An ethnographic account of the Venda dating to the 1930s relates that they possessed “several different varieties of old beads” which were “greatly prized by their owners on account of their age and rarity” and were “handed down as heirlooms”.<sup>33</sup>

## **5. Conclusion**

The identification of lead tin yellow Type I as the pigment coloring the yellow bead dates it as much older than the red bead. The appearance of the yellow bead, high corrosion level and glass composition fit in with this classification and the bead was most probably passed on to the owner by ancestors and kept as an heirloom. The pigment coloring the red bead was identified as nano-  $(\text{Zn,Cd})\text{S}_x\text{Se}_{x-1}$  mixed crystals, a pigment that was only widely used in the early 20<sup>th</sup> century. This date casts doubt on local oral tradition, which associates the brick-built structure from which the beads

were recovered with Manzinzi, a Venda chief who, according to contemporary reports, had already died in the 1880s. The more recent date for the red bead resolves the apparent dissonance between the oral and written records, suggesting that the building was probably erected and/or occupied sometime later by one of Manzinzi's successors.

## **Acknowledgements**

Jan Boeyens and Maria van der Ryst wish to thank their Unisa colleagues and students for assistance during fieldwork at Magoro Hill. Special thanks are due to Wim Biemond, who first drew our attention to the archaeological significance of the red beads, and to Pieter Snyman, who led the team that excavated the brick-built structure.

We gratefully acknowledge the financial support of the NRF, UNISA and the University of Pretoria.

## **References**

1. L.C. Prinsloo, A. Tournié, Ph. Colomban, *J. Archaeol. Sci.* 38(12) (2011) 3264
2. A. Tournie, L.C. Prinsloo, Ph. Colomban, *J. Raman Spectrosc.*, (2011) article in press.
3. L.C. Prinsloo, Ph. Colomban, *J. Raman Spectrosc.*, 39(1) (2008) 79.
4. W.M.D. Phophi, *Muvenda! Dzhenala ya birou ya Tshivenda* 8(2) (1981) 14-18.
5. R. Wessmann, *Berliner Missionsberichte* 23/24 (1890) 500-501.
6. P. Francis, Jr., *Asia's Maritime Bead Trade: 300 B.C. to the Present*, University of Hawai'i Press, Honolulu, 2002.
7. Ph. Colomban, 2004, Glasses, glazes and ceramics-Recognition of the ancient technology from the Raman spectroscopy in *Archaeology and art history*, Edwards H.G.M., Chalmers J.M.(Eds), Royal Society of Chemistry, UK, ch.13, p.192.

8. P. Vandenabeele, H.G.M. Edwards, L. Moens, *Chem. Rev.* 107 (3) (2007) 675.
9. I.M. Bell, R.J.H. Clark, P.J. Gibbs, *Spectrochim. Acta Part A*, 53 (1997) 2159.
10. B. Kirmizi, Ph. Colomban, B. Quette, 2010a, On-site analysis of Chinese Cloisonné enamels from fifteenth to nineteenth centuries, *J. Raman Spectrosc.*, 41 (2010) 780.
11. C. Pelosi, G. Agresti, U. Santamaria, E. Mattel, *e-PS*. 7 (2010) 108.
12. Ph. Colomban, G. Sagon, A. Louchi, H. Binous, N. Ayed, *Revue d'Archéométrie*, 25, (2001) 101.
13. J.L. Mass, M.T. Wypyski, M.T. Stone, *Archaeometry*, 44 (2002) 5.
14. L. Burgio, R.J.H. Clark, *Spectrochim. Acta Part A* 57 (2001) 1491.
15. L. Biek, J. Bayley, *World Archaeol.*, ii (1) (1979) 1.
16. J.C. Wang, Y. Yan, S.I. Zhang, X.B. Zhang, S.K. Hark, Investigation of the effective wavelength selection in the Raman scattering of CdSe quantum dots, ICORS' 2000, Wiley and Sons, Beijing, China, 2000, pp. 588-599.
17. M. Bouchard, D.C Smith, C. Carabatos-Nédelec, *Spectrochim. Acta, Part A*, 68 (2007) 1101.
18. R.R. Prabhu and M.A. Khadar, *Bull. Mater. Sci.* 31(3) (2008) 511.
19. V.M. Dzhagan, M.Y. Valakh, A.E. Raevskaya, A.L. Sroyuk, Kuchmiy and D.R.T. Zahn, *Nanotechnology* 19 (2008) 1.
20. M. Ivanda, Y. Bischof, G. Lermann, A. Materny and W. Kiefer, *J. Appl. Phys.* 82 (6) (1997) 3116.
21. T. Bischof, M. Ivanda, G. Lermann, A. Materny, W. Kiefer and J. Kalus, *J. Raman Spectrosc.* 27 (1996) 297.
22. T. Bischof, G. Lermann, B. Schreder, A. Materny, W. Kiefer and m. Ivanda, *J. Opt. Soc. Am.*, 14 (12) (1997) 3334.
23. P. Verma, G. Irmer and J. Monecke, *J. Phys. Condens. Matter* 12 (2000) 1097.
24. M. Thoury, J.K. Delaney, E. René de la Rie, M. Palmer, K. Morales, J. Kruger, *Applied Spectrosc.*, 65 (8) (2011) 939.
25. W.C. Butterman, R.D. Brown Jr. *Mineral Commodity Profiles: Selenium*, U.S. Department of the Interior, U.S. Geological Survey, Open-File Report 03-018.
26. Ph. Colomban, G. March, L. Mazerolles, T. Karmous, N. Ayed, A. Ennabli, H.J. Slim, *Raman Spectrosc.* 2003; 34: 205

27. Ph. Colomban, V. Milande, H. Lucas, *J. Raman Spectrosc.* 35 (2004) 68.
28. Ph. Colomban, A. Tournie, L. Bellot-Gurlet, *J. Raman Spectrosc.* 37 (8), (2006) 841.
29. M. Lenoir, A. Grandjean, S. Poissonnet, D.R. Neuville, *J. Non-Crystall. Solids* 355 (2009),1468.
30. A. Tournié, P. Ricciardi, Ph. Colomban, *Solid State Ionics* 2008, 179, 2142.
31. M. Wood, *J. Afr. Archaeol.*, 9(1) (2011).
32. F. Ohinata, *Southern Afr. Human.* 14 (2002) 23.
33. H.A. Stayt, *The BaVenda*, Oxford University Press, London, 1931.