



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

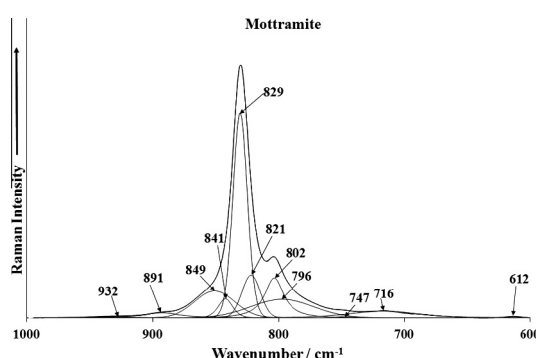
The molecular structure of the vanadate mineral mottramite [PbCu(VO₄)(OH)] from Tsumeb, Namibia – A vibrational spectroscopic study

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HIGHLIGHTS

- We have studied a mineral sample of mottramite PbCu(VO₄)(OH) from Tsumeb, Namibia.
- Chemical analysis using scanning electron microscopy with EDX shows complexity.
- Raman and infrared spectra were obtained.
- The complexity of the spectra is attributed to the chemical composition of the Tsumeb mottramite.
- Complexity of the spectra is attributed to symmetry reduction of the vanadate unit from T_d to C_s.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 22 August 2013

Received in revised form 11 November 2013

Accepted 13 November 2013

Available online 21 November 2013

Keywords:

Mottramite

Descloizite

Infrared spectroscopy

Raman microscopy

Pyromorphite

Apatite

ABSTRACT

We have studied a mineral sample of mottramite PbCu(VO₄)(OH) from Tsumeb, Namibia using a combination of scanning electron microscopy with EDX, Raman and infrared spectroscopy. Chemical analysis shows principally the elements V, Pb and Cu. Ca occurs as partial substitution of Pb as well as P and As in substitution to V. Minor amounts of Si and Cr were also observed. The Raman band of mottramite at 829 cm⁻¹, is assigned to the ν₁ symmetric (VO₄⁻) stretching mode. The complexity of the spectra is attributed to the chemical composition of the Tsumeb mottramite. The ν₃ antisymmetric vibrational mode of mottramite is observed as very low intensity bands at 716 and 747 cm⁻¹. The series of Raman bands at 411, 439, 451 cm⁻¹ and probably also the band at 500 cm⁻¹ are assigned to the (VO₄⁻) ν₂ bending mode. The series of Raman bands at 293, 333 and 366 cm⁻¹ are attributed to the (VO₄⁻) ν₄ bending modes. The ν₃, ν₃ and ν₄ regions are complex for both minerals and this is attributed to symmetry reduction of the vanadate unit from T_d to C_s.

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Introduction

Mottramite is a member of the descloizite group of minerals which are basic vanadates and are made up of minerals of the general formula PbM(VO₄)(OH) where M may be Cu (mottramite), Zn

(descloizite), Mn (pyrobelonite) or (Fe,Mn) (cechite) [1]. The minerals are of orthorhombic symmetry with *point group* *mmm* [1]. The minerals are built up of MO₄(OH)₂ tetragonal bipyramids of C_i site symmetry combined in chains along [001] connected to a framework of distorted vanadate tetrahedra of C_s symmetry and distorted PbO₈ square antiprisms [2,3]. The free vanadate ion has tetrahedral T_d symmetry [4]. Ross [5] reports the free aqueous vanadate ion as having a ν₁ (A₁) mode at 874 cm⁻¹, the ν₂ mode

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of E symmetry at 345 cm^{-1} , the ν_3 mode of F_2 symmetry at 855 cm^{-1} and the ν_4 mode also of F_2 symmetry at 345 cm^{-1} . For perfect T_d symmetry, the first two modes are Raman active/infrared inactive and the last two modes both Raman and infrared active. The presence of a cation in the aqueous vanadate solution as an ion pair reduces this symmetry.

Some information on the spectroscopy of the VO_4^- unit for the descloizite group is available [5,6]. Ross reported the infrared absorption spectra of descloizite with bands at 860, 750 and 453 cm^{-1} and attributed these bands to the ν_1 , ν_3 and ν_4 vibrational modes. The Raman spectrum of mottramite was not reported. The infrared spectra of vanadate minerals have been reported and the variation ascribed to the VO distances in the structure [7]. Griffiths [6] reported bands for the infrared spectra of descloizite at 865, 820, 777, 777, 760, 400, 384, 377, 356, 301 and 200 cm^{-1} . Mottramite had infrared absorption bands at 834, 802, 795, 358, 348, 331, 295, 288 and 188 cm^{-1} . No Raman spectra were reported in the work of Griffith [6]. Considerable differences in the infrared spectra of the two minerals were observed even though the two minerals had the same structure and symmetry. Such differences may be attributed to the vanadium–oxygen stretching and vanadium–oxygen bond–bond interaction force constants of the VO_4^- unit in the structure of minerals.

Raman spectroscopy has proven very useful for the study of minerals [8–11]. Indeed, Raman spectroscopy has proven most useful for the study of diagenetically related minerals as often occurs with minerals containing vanadate groups such as mottramite, descloizite, pyrobelonite and cechite. The objective of this research is to report the vibrational spectra of mottramite and to relate the spectra to the molecular structure of the mineral mottramite.

Experimental

Samples description and preparation

The mottramite sample studied in this work forms part of the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAC-099.

The sample was gently crushed and the associated minerals were removed under a stereomicroscope Leica MZ4. Scanning electron microscopy (SEM) in the EDS mode was applied to support the mineral characterization. The XRD pattern shows the mineral is a single phase with no impurities.

Scanning electron microscopy (SEM)

Experiments and analyses involving electron microscopy were performed in the Center of Microscopy of the Universidade Federal de Minas Gerais, Belo Horizonte, Minas Gerais, Brazil (<http://www.microscopia.ufmg.br>).

Mottramite crystals were coated with a 5 nm layer of evaporated carbon. Secondary Electron and Backscattering Electron images were obtained using a JEOL JSM-6360LV equipment. Qualitative and semi-quantitative chemical analyses in the EDS mode were performed with a ThermoNORAN spectrometer model Quest and were applied to support the mineral characterization.

Raman spectroscopy

The crystals of mottramite were placed and oriented on the stage of an Olympus BHSM microscope, equipped with $10\times$ and $50\times$ objectives and part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a Charge Coupled Device (CCD). Raman spectra were excited

by a HeNe laser (633 nm) at a nominal resolution of 2 cm^{-1} in the range between 100 and 4000 cm^{-1} . Details of the experimental procedure have been published. The spatial resolution of the instrument is $1\text{ }\mu\text{m}$. Thus, if crystals are less than this value, a mixture of crystals will be measured. However, the crystals of mottramite used in this experiment were $>1.1\text{ }\mu\text{m}$.

Infrared spectroscopy

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the $4000\text{--}525\text{ cm}^{-1}$ range were obtained by the co-addition of 128 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm/s . Spectra were co-added to improve the signal to noise ratio.

Spectral manipulation such as baseline adjustment, smoothing and normalization were performed using the Spectralcalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package which enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentz–Gauss cross-product function with the minimum number of component bands used for the fitting process. The Gauss–Lorentz ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.995.

Results and discussion

Chemical characterization

The SEM/BSI image of the mottramite crystal aggregate studied in this work is shown in Fig. 1. The sample shows a complex chemical composition. The major elements are V, Pb and Cu. Ca occurs as partial substitution of Pb as well as P and As in substitution to V. Minor amounts of Si and Cr were also observed (Fig. 2).

Vibrational spectroscopy of mottramite

The Raman spectrum of mottramite over the $4000\text{--}100\text{ cm}^{-1}$ spectral range is reported in Fig. 3a. This figure displays the position and relative intensities of the Raman bands. It is noted that there is very little intensity in the OH stretching region. Hence, the Raman spectrum is subdivided into sections for more detail

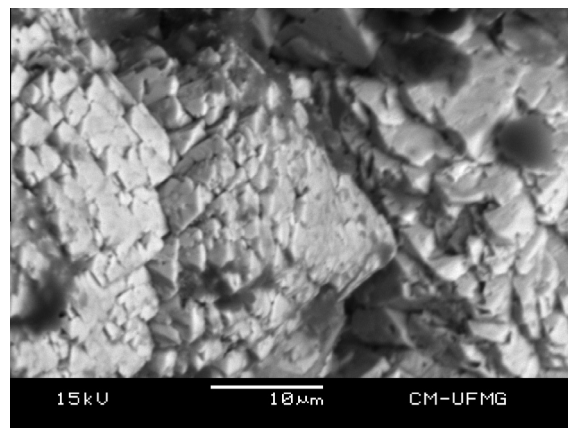


Fig. 1. Backscattered electron image (BSI) of a mottramite single crystal up to 0.5 mm in length.

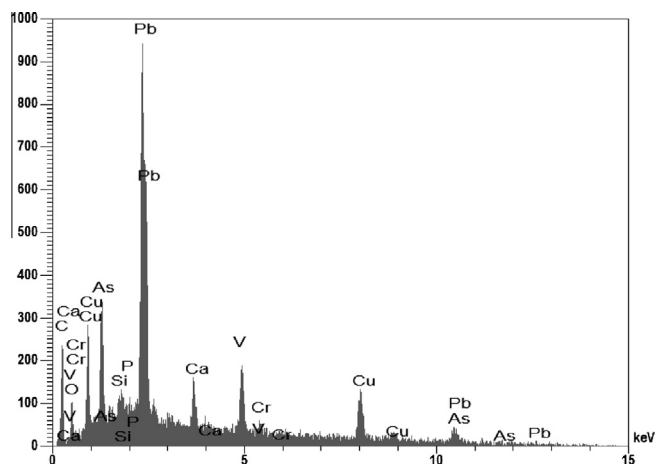


Fig. 2. EDS analysis of mottramite.

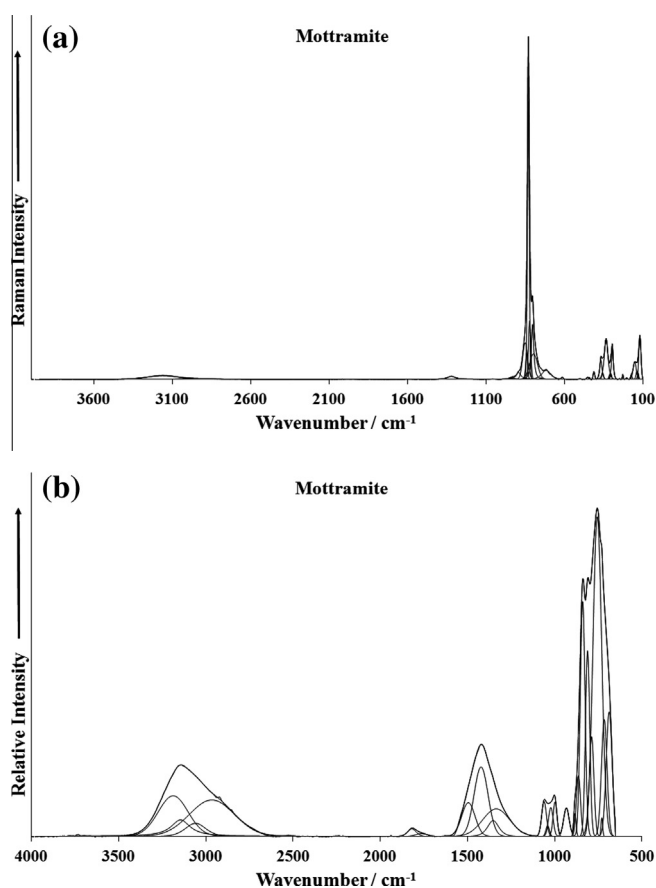


Fig. 3. (a) Raman spectrum of mottramite over the 4000–100 cm^{-1} spectral range. (b) Infrared spectrum of mottramite over the 4000–500 cm^{-1} spectral range.

based upon the type of vibration being studied. The infrared spectrum of mottramite over the 4000–500 cm^{-1} spectral range is reported in Fig. 3b. This spectrum shows the position and relative intensities of the infrared bands. In a similar fashion to the Raman spectrum, the infrared spectrum is subdivided into sections for a more detailed study.

The Raman spectrum of mottramite over the 600–1000 cm^{-1} spectral range is shown in Fig. 4a. The spectrum is dominated by a very intense band at 829 cm^{-1} which is assigned to the symmetric stretching mode (ν_1) of VO_4^- of mottramite. Some low intensity

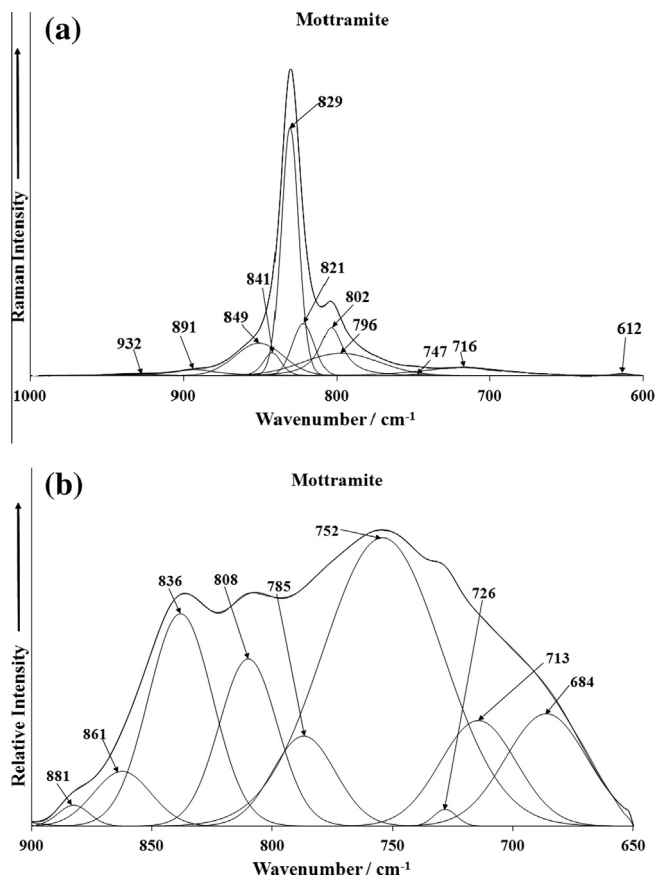


Fig. 4. (a) Raman spectrum of mottramite over the 1000–600 cm^{-1} spectral range. (b) Infrared spectrum of mottramite over the 900–650 cm^{-1} spectral range.

shoulders are observed at 802, 821 and 849 cm^{-1} . The complexity of the chemical analysis is reflected in the multiple bands observed in this spectral region. Other low intensity Raman bands are found at 612, 716 and 747 cm^{-1} . The position of this band may be compared with the Raman band of descloizite observed at 844 cm^{-1} [12]. The differences in the symmetric stretching region of mottramite and descloizite are attributed to the differences in the replacement of the Pb for Zn in the descloizite example and the replacement of Pb with Cu and Ca in the mottramite case. Substitution of the Zn by Cu has caused an increase in the interatomic interactions on the vanadate units [12]. Replacement of the Zn by Cu has caused the internal modes of the vanadate unit to correlation couple with the same modes of another vanadate unit [12].

The infrared spectrum of mottramite is illustrated in Fig. 4b. This spectrum is broad and may be resolved into component bands at 684, 713, 726, 752, 898, 836, 861 and 881 cm^{-1} . The antisymmetric stretching mode (ν_3) of VO_4^- of mottramite is readily observed in the infrared spectrum as the infrared bands at 726, 752 and 785 cm^{-1} . This observation is unusual as three bands are found when six bands are expected. The intense Raman band at 829 cm^{-1} is reflected in the infrared band at 836 cm^{-1} . It is probable that the very low intensity Raman bands at 716 and 747 cm^{-1} are due to the antisymmetric stretching mode (ν_3) of VO_4^- of mottramite. Comparing the Raman spectrum of descloizite and mottramite, all vanadate units are crystallographically equivalent. This suggests that both the Zn and Cu cations exist in the mottramite sample and according to their relative proportions and local distributions, the vibrational selection rules may be modified or relaxed. I.e. there are two sets of overlapping bands 829/821 cm^{-1} and 802/796 cm^{-1} . Such a result may arise from the separate detection of vanadate in association with either the Cu or the Zn.

The Raman spectra of mottramite over the 550–100 cm^{-1} spectral range are reported in Fig. 5. This spectral region includes the bending modes of the vanadate unit (ν_2) and the ν_4 vibrational modes. Ross [5] reports the bending mode of the vanadate ion as an infrared band at 460 cm^{-1} . The equivalent band in the Raman is observed at 411 cm^{-1} . The most intense band in the Raman spectrum of mottramite is observed at 333 cm^{-1} with other intense bands at 293 and 366 cm^{-1} . The series of Raman bands of mottramite at 411, 439, 451 and 500 cm^{-1} are assigned to the ν_2 bending mode. Hence, the other bands observed in this region at 366, 333 and 293 cm^{-1} are attributable to the ν_4 vibration. The Raman bands between 100 and 250 cm^{-1} are simply described as external lattice modes.

The Raman spectrum of mottramite over the 3600–2600 cm^{-1} spectral range is provided in Fig. 6a. This figure shows a broad Raman band at 3162 cm^{-1} with a shoulder at 2927 cm^{-1} . The infrared spectrum of mottramite shows a broad spectral profile with resolved infrared bands at 2963, 3056, 3142 and 3184 cm^{-1} . These bands are attributed to the stretching vibrations of the OH units. These bands are associated with the substituting metal in the vanadate structure. The hydroxyl deformation modes (Zn–OH and Cu–OH) are not observed in the Raman spectra but may be observed in the infrared spectrum. In a previous study infrared bands were observed in the 506–508 cm^{-1} region and these bands were assigned to CuO stretching vibrations. However, a more likely assignment is to the M–OH deformation modes. No infrared or Raman bands were observed in the 1600–1700 cm^{-1} spectral region; thus, indicating that no water was present in the sample.

The results of the Raman spectra of the Tsumeb mottramite show that the wavenumbers of the stretching and bending vibrations of mottramite are influenced by the forces exerted on the vanadate unit in the crystal structure. Substitution of Cu^{2+} and Ca^{2+} for Zn^{2+} in the structure affects the internal force field of the vanadate unit. This results in the complexity of the Raman and infrared spectra of the Tsumeb mottramite. The crystal structure of the mottramite-descloizite series has the Pb^{2+} cation coordinated by seven anions between 2.45 and 2.80 Å with a further two anions distant at 3.195 Å. The Zn^{2+} or Cu^{2+} cation is coordinated by six anions in a distorted octahedral arrangement with a CuO distance of 2.112 Å. X-ray diffraction shows that the mottramite and descloizite form an isomorphous series.

Careful single crystal X-ray structural analyses of both mottramite and descloizite have been reported. These have included bond valence calculations and attention has been drawn explicitly to differences in the VO_4^{3-} geometries in these and a variety of other vanadates. Subtle differences in the two structures are associated

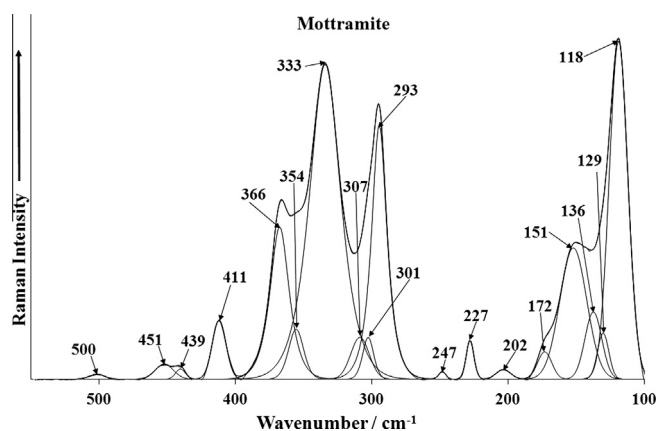


Fig. 5. Raman spectrum of mottramite over the 550–100 cm^{-1} spectral range.

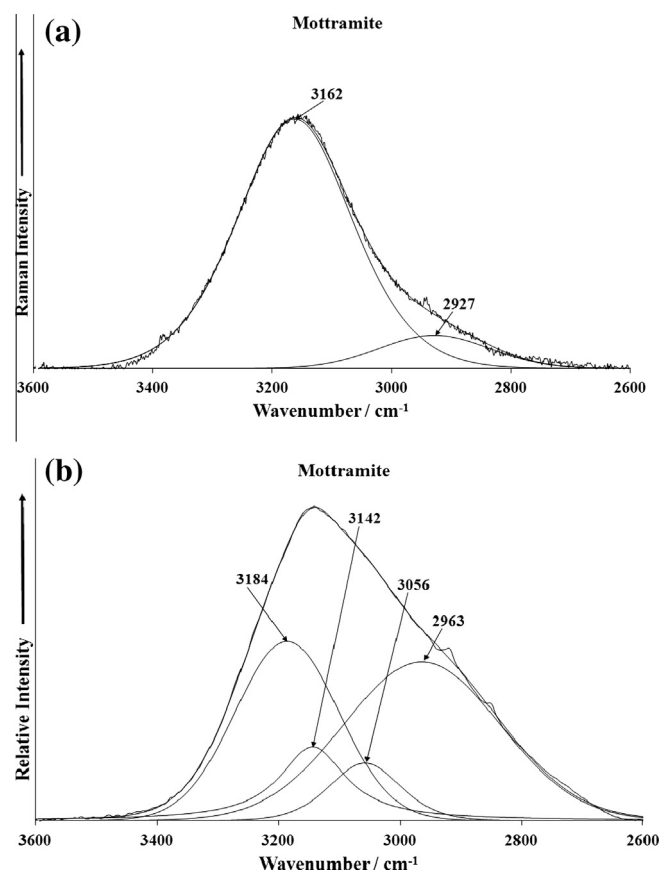


Fig. 6. (a) Raman spectrum of mottramite over the 3600–2600 cm^{-1} spectral range. (b) Infrared spectrum of mottramite over the 3600–2600 cm^{-1} spectral range.

with the Jahn–Teller distortion of the M site as Cu^{2+} is substituted for Zn^{2+} and these affect, in turn, the geometrical details of the vanadate unit and in turn results in the complexity of the vibrational spectra. Furthermore because of the changing bond order of vanadate and Cu^{2+} versus Zn^{2+} , the force constants for the V–O bonds must alter. Thus, just as the OH modes are different in the two minerals, and two are detected apparently as the result of the presence of both Pb^{2+} and Cu^{2+} in the mottramite sample, additional bands associated with the VO_4^{3-} unit may be attributed to local perturbations in the structure associated in turn with localized Cu^{2+} – VO_4^{3-} and Zn^{2+} – VO_4^{3-} interactions.

Conclusions

We have used a combination of Raman and infrared spectroscopy to explore the structure of the vanadate mineral mottramite. The Raman spectrum is dominated by a very intense band at 829 cm^{-1} assigned to the symmetric stretching mode (ν_1) of VO_4^{3-} of mottramite. Some low intensity Raman bands are observed at 802, 821 and 849 cm^{-1} . The complexity of the chemical analysis is reflected in the multiple bands observed in this spectral region. Other low intensity Raman bands are found at 612, 716 and 747 cm^{-1} . These bands are attributed to the antisymmetric stretching mode (ν_3) of VO_4^{3-} of mottramite. The observation of multiple low intensity bands suggests that both the Zn and Cu cations exist in the mottramite sample and according to their relative proportions and local distributions, the vibrational selection rules may be modified or relaxed.

Acknowledgements

The financial and infra-structure support of the Discipline of Nanotechnology and Molecular Science, Science and Engineering Faculty of the Queensland University of Technology, is gratefully acknowledged. The Australian Research Council (ARC) is thanked for funding the instrumentation. The authors would like to acknowledge the Center of Microscopy at the Universidade Federal de Minas Gerais (<http://www.microscopia.ufmg.br>) for providing the equipment and technical support for experiments involving electron microscopy. The authors are also grateful to CNPq Project 402852/2012-5. Livia Corrêa is grateful to CAPES – Programa Jovens Talentos.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.saa.2013.11.086>.

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