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Vibrational spectroscopic characterization of the sulphate mineral khademite $Al(SO_4)F{\cdot}5(H_2O)$

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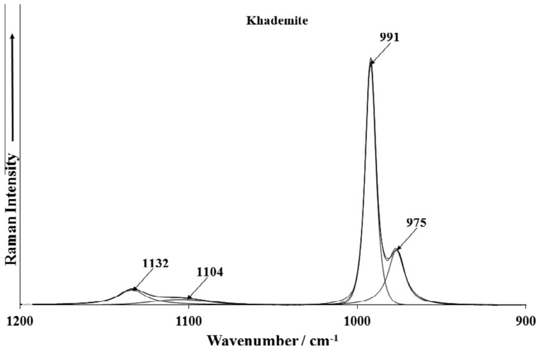
HIGHLIGHTS

- We have studied the sulphate mineral khademite $Al(SO_4)F{\cdot}5(H_2O)$.
- Using vibrational spectroscopy.
- The observation of multiple water stretching vibrations gives credence to the non-equivalence of water units.
- Vibrational spectroscopy enables an assessment of the structure of khademite.

GRAPHICAL ABSTRACT



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ABSTRACT

Vibrational spectroscopy has been used to characterize the sulphate mineral khademite Al(SO4)F·5(H2O). Raman band at 991 cm−1 with a shoulder at 975 cm−1 is assigned to the v1 (SO4)2− symmetric stretching mode. The observation of two symmetric stretching modes suggests that the sulphate units are not equivalent. Two low intensity Raman bands at 1104 and 1132 cm−1 are assigned to the v3 (SO4)2− antisymmetric stretching mode. The broad Raman band at 618 cm−1 is assigned to the v4 (SO4)2− bending modes. Raman bands at 455, 505 and 534 cm−1 are attributable to the doubly degenerate v2 (SO4)2− bending modes. Raman bands at 2991, 3146 and 3380 cm−1 are assigned to the OH stretching bands of water. Five infrared bands are noted at 2458, 2896, 3203, 3348 and 3489 cm−1 are also due to water stretching bands. The observation of multiple water stretching vibrations gives credence to the non-equivalence of water units in the khademite structure. Vibrational spectroscopy enables an assessment of the structure of khademite.

Introduction

The mineral khademite is a fluorinated hydrated sulphate of aluminium of formula $Al(SO_4)F{\cdot}5(H_2O)$ [1,2]. It is rarely formed in the oxidized zone of hydrothermal base-metal deposits [3]. This mineral is known from a number of places in Australia, including the Kintore open Cut Mine at Broken Hill, NSW, Australia. The mineral is associated with other fluorinated sulphates namely wilcoxite $MgAl(SO_4)_2F{\cdot}18(H_2O)$, lannonite $HCa_4Mg_2Al_4(SO_4)_8F_9{\cdot}32(H_2O)$ [4].

This sulphate mineral is found in many parts of the world including from Saghand, Yazd, Iran; at the Rammelsberg mine, near Goslar, Harz Mountains, Germany; in the Cetine mine, 20 km southwest of Siena, Tuscany, Italy; from the Schoeller mine, Libušin, near Kladno, Czech Republic and in the Lone Pine mine, Wilcox district, near Silver City, Catron Co., New Mexico, USA. Khademite [4,5] is associated with copiapite, amarantite,

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parabutlerite, butlerite, jarosite (Saghand, Iran); wilcoxite, lannonite, gypsum (Lone Pine mine, New Mexico, USA). The mineral type locality is from Saghand, Iran.

The mineral [3] is orthorhombic with *Point Group: 2/m 2/m 2/m.* The cell data is *Space Group: Pcab.* $a = 11.181(4)$, $b = 13.048(5)$, $c = 10.885(4)$, with $Z = 8$. According to Bachet et al. [3] the structure consists of discrete SO_4 tetrahedra, Al(Ow)6 and Al(Ow)4F2 octahedra connected by a network of H bonds. Al atoms are in special positions 4(*a*) and 4(*b*) and the corresponding octahedra form sheets parallel to (100); they alternate with SO_4 tetrahedra.

This paper is a part of systematic studies of vibrational spectra of minerals of secondary origin in the oxide supergene zone. In this work, we attribute bands at various wavenumbers to vibrational modes of khademite using Raman spectroscopy complemented with infrared spectroscopy and relate the spectra to the structure of the mineral.

Experimental

Samples description and preparation

The khademite sample studied in this work was collected from Kladno Mine, Central Bohemia Region, Czech Republic [6]. The mineral occurs as efflorescence covering the weathered rock. The individual crystals show prismatic habitus. The sample was incorporated into the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAB-079. The sample was gently crushed and the associated minerals were removed under a stereomicroscope Leica MZ4.

Raman microprobe spectroscopy

Crystals of khademite were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10×, 20×, and 50× objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a CCD detector (1024 pixels). The Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser producing highly polarized light at 633 nm and collected at a nominal resolution of $2\ cm^{-1}$ and a precision of $\pm 1\ cm^{-1}$ in the range between 200 and $4000\ cm^{-1}$. Repeated acquisitions on the crystals using the highest magnification (50×) were accumulated to improve the signal to noise of the spectra. Raman Spectra were calibrated using the $520.5\ cm^{-1}$ line of a silicon wafer. The Raman spectrum of at least 10 crystals was collected to ensure the consistency of the spectra.

A spectrum of khademite is given in the RRUFF data base at http://rruff.info/Khademite.

This spectrum suffers from a lack of signal. No band assignments are provided and no assessment of the OH stretching region is shown. The downloaded spectrum is reported in the Supplementary information as Fig. S1.

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 $4000–525\ cm^{-1}$ 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. The infrared spectra are given in the Supplementary information.

Spectral manipulation such as baseline correction/adjustment and smoothing were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package that 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 Lorentzian–Gaussian cross-product function with the minimum number of component bands used for the fitting process. The Gaussian–Lorentzian 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

Vibrational Spectroscopy

The mineral khademite contains both sulphate and fluoride anions, and therefore, the presence of these anions may be observed using vibrational spectroscopy. Certainly any oxyanion may be observed. It should be noted that the fluoride anion and the hydroxyl anion are about equal in size and in nature one may repalce the other in mineral structures. As the structure and formula of khademite was researched, there was considerable arguement about its true formula.

The fluoride anion is much more difficult to detect using vibrational spectroscopy. A good starting point to study the position of the expected bands and to observe where the bands occur in aqueous solutions and then to observe the position of the bands resulting from the vibrational spectroscopy of minerals containing the individual anions. In aqueous systems, the sulphate anion is of *T*d symmetry and has symmetric stretching mode (ν_1) at $981\ cm^{-1}$, the antisymmetric stretching mode (ν_3) at $1104\ cm^{-1}$,the symmetric bending mode (ν_2) at $451\ cm^{-1}$ and the ν_4 mode at $613\ cm^{-1}$ [5]. In aqueous systems, Raman spectra of phosphate oxyanions show a symmetric stretching mode (ν_1) at $938\ cm^{-1}$, the antisymmetric stretching mode (ν_3) at $1017\ cm^{-1}$, the symmetric bending mode (ν_2) at $420\ cm^{-1}$ and the ν_4 mode at $567\ cm^{-1}$ [5].

S.D. Ross in Farmer's treatise [7] reported the infrared spectra of the jarosite–alunite minerals (Table 18.IX page 433). This table compares the infrared spectra of minerals from the alunite–jarosite supergroups. Ross reported infrared bands for sulphate containing alunite at $1030\ cm^{-1}$ (ν_1), $475\ cm^{-1}$ (ν_2), 1086, $1170\ cm^{-1}$ (ν_3), 605, $632\ cm^{-1}$ (ν_4). OH vibrations were reported at 3485 and 505,780,802 cm^{-1} attributed to the stretching and bending of the OH units. Infrared bands for jarosite 1018, $1028\ cm^{-1}$ (ν_1), $482\ cm^{-1}$ (ν_2), 1100, $1190\ cm^{-1}$ (ν_3), 638, $685\ cm^{-1}$ (ν_4). OH vibrations for jarosite were reported at 3260, 3355, 3430 and 512,790 cm^{-1} attributed to the stretching and bending of the OH units. Raman spectra of these minerals have also been published [8–11]. These results serve to show the positions of the bands which may be assigned to sulphate and phosphate.

Vibrational spectroscopy

The Raman spectrum of khademite $Al(SO_4)F{\cdot}5(H_2O)$ over the $100–4000\ cm^{-1}$ spectral range is illustrated in Fig. 1a. This spectrum shows the position and relative intensities of the Raman bands. It is noteworthy that there are large parts of the spectrum where little or no intensity is observed and therefore the spectrum is subdivided into sections based upon the type of vibration being studied. The infrared spectrum of khademite over the $500–4000\ cm^{-1}$ spectral range is reported in Fig. 1b. This spectrum shows the position and relative intensity of the infrared bands. A comparison between the Raman and infrared spectra of khademite may be achieved.

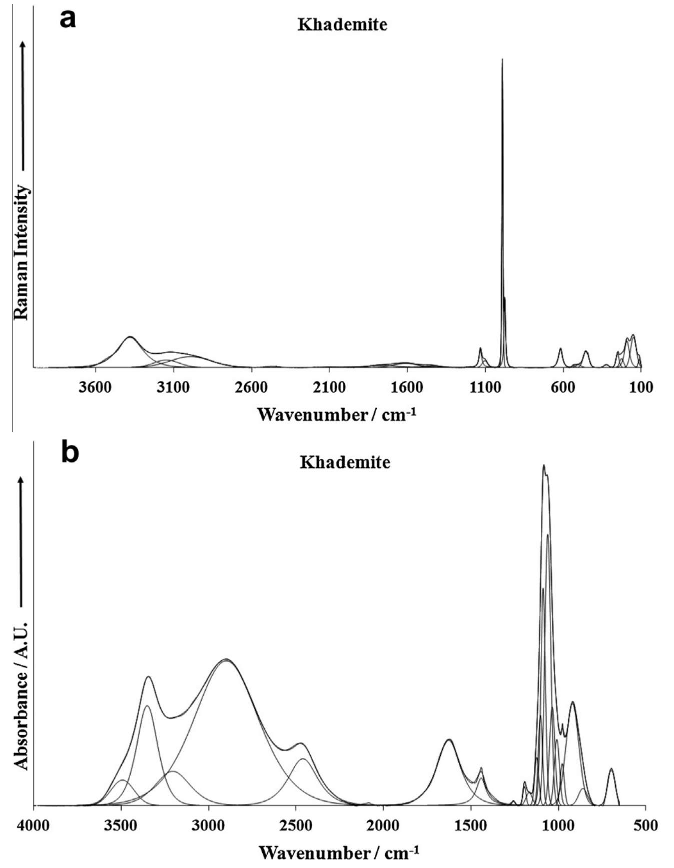

Fig. 1. (a) Raman spectrum of khademite over the 100–4000 cm^{-1} spectral range. (b) Infrared spectrum of khademite over the 500–4000 cm^{-1} spectral range.

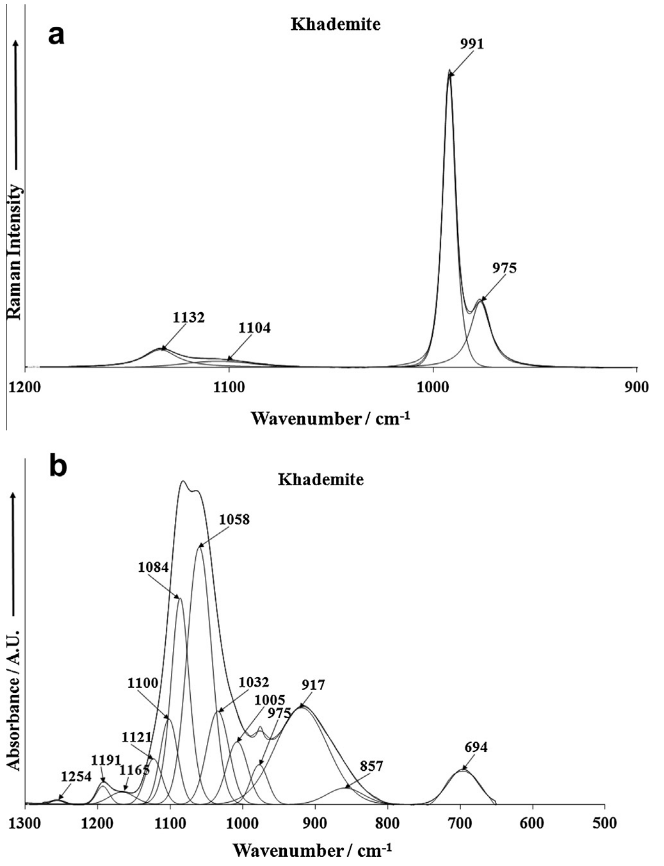

Fig. 2. (a) Raman spectrum of khademite over the 800–1400 cm^{-1} spectral range. (b) Infrared spectrum of khademite over the 500–1300 cm^{-1} spectral range.

The Raman spectrum of khademite in the 900–1200 cm^{-1} spectral range is shown in Fig. 2a. An intense Raman band at 991 cm^{-1} is assigned to the ν_1 $(SO_4)^{2-}$ symmetric stretching mode. A second band is observed at 975 cm^{-1} and may also be attributed to this vibrational mode. It is noted that in the Raman spectrum on the RRUFF data base http://rruff.info/Khademite shows two strong sharp bands at around 981 and 990 cm^{-1}.

The observation of two symmetric stretching modes suggests that the sulphate units are not equivalent. Perhaps, one sulphate unit is associated with the fluoride anion. Two low intensity Raman bands at 1104 and 1132 cm^{-1} are assigned to the ν_3 $(SO_4)^{2-}$ antisymmetric stretching mode. In the Raman spectrum of khademite from the RRUFF data base, two strong Raman bands are noted at 1151 and 1176 cm^{-1} which are attributed to this antisymmetric stretching mode.

The infrared spectrum over the 500 to 1300 cm^{-1} spectral range is reported in Fig. 2b. The spectrum shows a complex set of overlapping bands, The most intense bands found at 1058 and 1084 cm^{-1}are attributed to the ν_3 $(SO_4)^{2-}$ antisymmetric stretching mode. Other infrared bands at 1100, 1121, 1165 and 1181 cm^{-1} may also be attributed to this vibration. The two infrared bands at 975 and 1005 cm^{-1} may be attributed to the ν_1 $(SO_4)^{2-}$ symmetric stretching mode. It is thought that the infrared band at 917 cm^{-1} is associated with water and may be attributed to the water librational mode.

The Raman spectrum of khademite in the 300 to 800 cm^{-1} spectral range and in the 100 to 300 cm^{-1} spectral range is reported in Fig. 3. The broad Raman band at 618 cm^{-1} which may be composed of multiple overlapping bands is assigned to the ν_4 $(SO_4)^{2-}$ bending modes. In the RRUFF spectrum, an intense band is observed at exactly this position. In this RRUFF spectrum, a band is noted at 823 cm^{-1} which was not detected in this work. The Raman bands at 455, 505 and 534 cm^{-1} are attributable to the doubly degenerate ν_2 $(SO_4)^{2-}$ bending modes. The RRUFF spectrum of khademite suffers from a lack of signal; nevertheless a band may be observed at 441 cm^{-1} with other bands observed on the higher wavenumber side of this band.

It is thought that the Raman band at 324 cm^{-1} is due to the AlO stretching vibration. The series of overlapping bands in Fig. 3b are simply described as lattice vibrations.

The Raman spectrum in the 2600–3800 cm^{-1} spectral range is reported in Fig. 4a. The infrared spectrum over the 2000–3800 cm^{-1} spectral range is shown in Fig. 4b. The Raman bands at 2991, 3146 and 3380 cm^{-1} are assigned to the OH stretching bands of water. Five infrared bands are noted at 2458, 2896, 3203, 3348 and 3489 cm^{-1} are also due to water stretching bands. The observation of multiple water stretching vibrations gives credence to the non-equivalence of water units in the khademite structure. The position of the bands at quite relatively low wavenumber positions (e.g. 2458, 2896) indicates very strong hydrogen bonding in the khademite structure.

The Raman spectrum of khademite in the 1300–1900 cm^{-1} is reported in Fig. 5a. The spectrum suffers from a lack of signal, nevertheless a band may be observed at 1609 cm^{-1} and is ascribed to the water bending mode. The infrared spectrum of khademite over the 1300–2000 cm^{-1} spectral range is shown in Fig. 5b. A broad band at 1625 cm^{-1} is noted and assigned to the water bending mode. Another band is seen at 1439 cm^{-1}. It is not known what this band may be assigned.

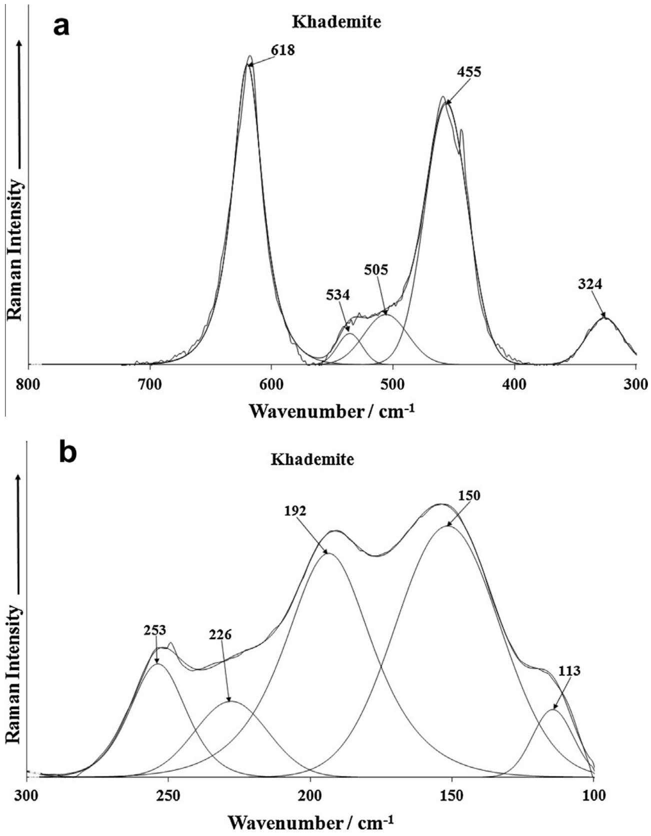

Fig. 3. (a) Raman spectrum of khademite over the 300–800 cm^{-1} spectral range. (b) Raman spectrum of khademite over the 100–300 cm^{-1} spectral range.

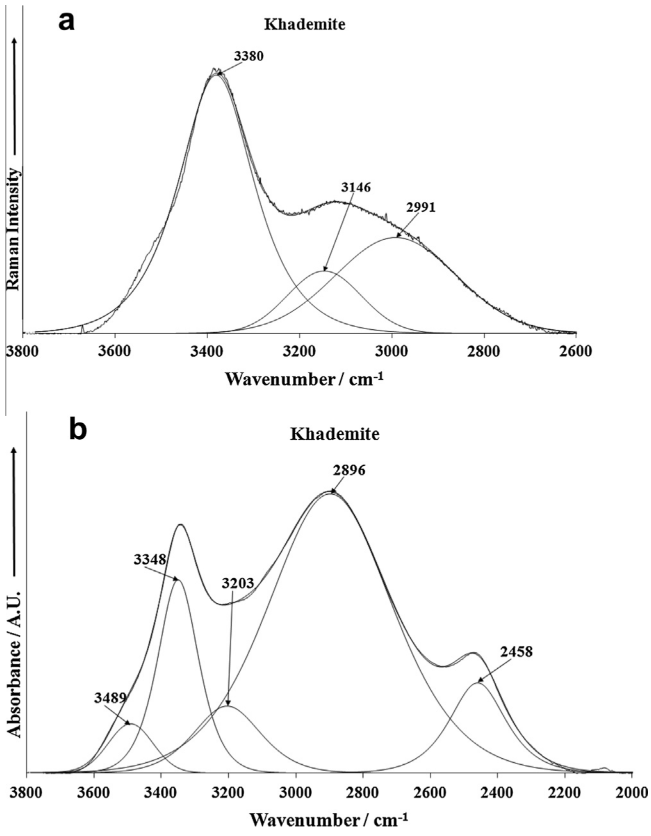

Fig. 4. (a) Raman spectrum of khademite over the 2600–4000 cm^{-1} spectral range. (b) Infrared spectrum of khademite over the 2600–4000 cm^{-1} spectral range.

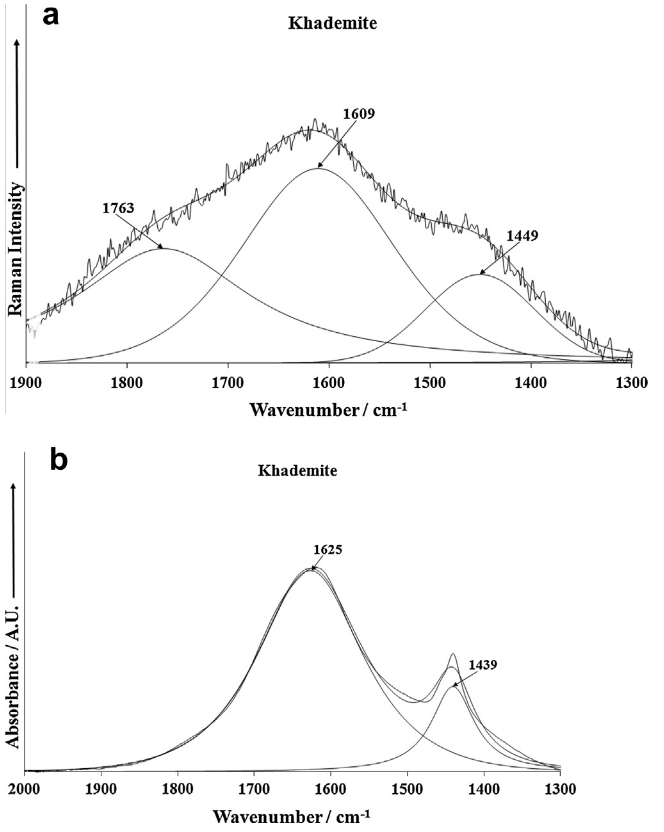

Fig. 5. (a) Raman spectrum of khademite over the 1300–1800 cm^{-1} spectral range. (b) Infrared spectrum of khademite over the 1300–1800 cm^{-1} spectral range.

Conclusions

A combination of Raman spectroscopy at ambient temperature complimented with infrared spectroscopy has been used to characterise the sulphate mineral known as khademite $Al(SO_4)F{\cdot}5(H_2O)$ originating from Kladno Mine, Central Bohemia Region, Czech Republic. Khademite is one of a very few fluorinated sulphate minerals including wilcoxite $MgAl(SO_4)_2F{\cdot}18(H_2O)$, lannonite $HCa_4Mg_2Al_4(SO_4)_8F_9{\cdot}32(H_2O)$. Multiple symmetric stretching modes are observed and support the concept of the non-equivalent sulphate units in the khademite structure. The observation of multiple water stretching vibrations gives credence to the non-equivalence of water units in the khademite structure. The position of the bands at quite relatively low wavenumber positions (e.g. 2458, 2896) indicates very strong hydrogen bonding in the khademite structure.

Acknowledgments

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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.2013.07.020.

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