Raman and infrared spectroscopic study of the mineral goyazite SrAl$_3$(PO$_4$)$_2$(OH)$_5$·H$_2$O

Andrés López, Yunfei Xi, Ray L. Frost,

School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology, GPO Box 2434, Brisbane Queensland 4001, Australia.

Abstract

We have studied the mineral goyazite using Raman and infrared spectroscopy. Goyazite is a member of the crandallite subgroup of the alunite supergroup. The crystal structure is of the alunite-type and consists of sheets of corner-sharing AlO$_6$ octahedra parallel to (0001). The octahedrally coordinated Sr$^{2+}$ cations occupy cavities between pairs of octahedral sheets and are surrounded by six oxygen atoms from the (Al$^{3+}$)O$_6$ octahedra.

The very intense sharp band at 983 cm$^{-1}$ is assigned to the $\nu_1$ PO$_4$$^{3-}$ symmetric stretching mode. The observation of a single band supports the concept that all the phosphate units are equivalent in the structure of goyazite. Raman bands observed at 1029 cm$^{-1}$ and 1037 cm$^{-1}$ are assigned to the $\nu_3$ PO$_4$$^{3-}$ antisymmetric stretching vibrations. Two Raman bands at 895 and 927 cm$^{-1}$ are attributed to the stretching vibrations of H$_2$PO$_4$; thus indicating some hydrogen phosphate units in the structure of goyazite. Raman bands at 556, 581, 596 and 612 cm$^{-1}$ are assigned to the $\nu_4$ PO$_4$$^{3-}$ bending modes, suggesting a reduction of symmetry of phosphate units. Two sharp Raman bands at 3609 and 3631 cm$^{-1}$ are attributed to OH stretching vibrations from the goyazite hydroxyl units. Broad Raman bands at 2924, 3043, 3210, 3429 and 3511 cm$^{-1}$ are assigned to water stretching vibrations. Vibrational spectroscopy enables subtle details of the molecular structure of goyazite to be determined.

Keywords: Raman spectroscopy, goyazite, crandallite, phosphate

* Author to whom correspondence should be addressed (r.frost@qut.edu.au)
Introduction

Minerals of the crandallite mineral group are many and varied [1-3]. The crandallite group forms a large family of isostructural compounds having the general formula $A B_3(XO_4)(OH, H_2O)_6$, where $A = M^+, M^{2+}, M^{3+}$ and/or $M^{4+}$ cations, $B = M^{3+}$ (and minor $M^{2+}$ cations, such as $Cu^{2+}$, $Zn^{2+}$ and $M^{5+}$, such as $Nb^{5+}$ and $Ta^{5+}$), and $X = P^{5+}, As^{5+}, S^{6+}, Cr^{6+}$ and minor $Si^{4+}$ [4]. Goyazite $SrAl_3(PO_4)_2(OH)_5\cdot H_2O$ [3] is one of the crandallite mineral group consisting of a granular yellowish white hydrous strontium aluminium phosphate. The mineral is renowned for the content of rare earth elements. The mineral is named after the province of Goyaz, Brazil [5, 6]. There are some discrepancies in its chemical formula reported in the literature $SrAl^{3+}_3(PO_4)_3(OH)_5$ [7], $SrAl_3(PO_4)_2(OH, H_2O)_6$ [4, 8]. Walenta [9] ascribed the chemical formula $BaFe_3H(AsO_4)_2(OH)_6$ for dussertite and later [10] $BaFe_3(AsO_4)_2(OH)_5\cdot H_2O$. This agrees with the formula published by Winchell and Winchell [11] and Fleischer et al. [12]. Whether the formula of goyazite is $SrAl_3(PO_4)_2(OH)_5\cdot H_2O$ or is $SrAl_3(H PO_4,PO_4)_2(OH)_6$ is open to question. However, vibrational spectroscopy should be able to solve whether water is involved in the formula or not. Indeed vibrational spectroscopy can define what type of phosphate units are in the goyazite structure.

The mineral is hexagonal with Point Group: $3\overline{2}/m$ and forms rhombohedral crystals up to 2 cm [13, 14]. Goyazite is isostructural with alunite. The colour of goyazite varies from colourless, pink, lilac, honey-yellow, through to orange and varies according to the chemical composition. The crystal structure is of the alunite-type and consists of sheets of corner-sharing $(Al)O_6$ octahedra parallel to (0001). The octahedrally coordinated $Sr^{2+}$ cations occupy cavities between pairs of octahedral sheets and are surrounded by six oxygen atoms from the $(Al^{3+})O_6$ octahedra. The possible presence of $(AsO_3OH)^2-$ in the crystal structure of goyazite was not inferred from the structure analysis. On the contrary, in the refined crystal structure of analogous phosphate - gorceixite, the presence of $(PO_3OH)^2-$ groups was inferred in the disordered tetrahedral position of its crystal structure.

The mineral has been identified in a claystone from the Illawarra Coal Measures and in dike clays from the southern part of the Sydney Basin [15]. Goyazite-gorceixite is often
found in coal deposits [16-19]. Goyazite is a listed mineral found in soils [20]. The minerals are known for their rare earth content [21-24]. Very few vibrational spectroscopic studies of the crandallite minerals have been published. Breitinger et al. reported the spectra of a series of synthetic crandallites [25]. Gevorkyan et al. published the infrared and XRD of selected crandallite minerals [26].

The aim of this paper is to report the Raman spectra of goyazite, and to relate the spectra to the molecular and crystal chemistry of this phosphate mineral. The paper follows the systematic research on Raman and infrared spectroscopy of secondary minerals containing oxy-anions formed in the oxidation zone.

**Experimental**

**Minerals**

The mineral goyazite was supplied by The Mineralogical Research Company. Details of the mineral have been published [27]. Goyazite samples were obtained from (a) Sadisdorf, Schmiedeberg, Erzgebirge, Saxony, Germany (b) Kovdor Massif, Kola Peninsula, Murmanskaja Oblast, Northern Region, Russia (c) Alto Bernadino, Picui, Paraiba, Brazil. The mineral sample from Russia was selected for the reporting of the spectra as this mineral showed the cleanest spectra.

A spectrum of goyazite was also downloaded from the RRUFF data base. This mineral sample originated from Royal Ontario Museum (Museum sample M52410), Canada. The spectra are given in the supplementary information as Figures S1, S2, S3.

**Raman spectroscopy**

Crystals of goyazite were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x, 20x, and 50x 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 polarised light at 633 nm and collected at a nominal resolution of 2 cm\(^{-1}\) and a precision of ± 1 cm\(^{-1}\) in the range between 100 and 4000 cm\(^{-1}\). Repeated acquisition on the crystals using the highest magnification (50x) was accumulated to improve the signal to noise ratio in the spectra. Spectra were calibrated using the 520.5 cm\(^{-1}\) line of a silicon wafer.
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.

Band component analysis was undertaken using the Jandel ‘Peakfit’ (Erkrath, Germany) software package which enabled the type of fitting function to be selected and allowed 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 Lorentz-Gauss ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations (\(r^2\)) greater than 0.995. Band fitting of the spectra is quite reliable providing there is some band separation or changes in the spectral profile.

Results and discussion

Background

Raman spectra of aqueous phosphate oxyanions show a symmetric stretching mode (\(\nu_1\)) at 938 cm\(^{-1}\), the antisymmetric stretching mode (\(\nu_3\)) at 1017 cm\(^{-1}\), the symmetric bending mode (\(\nu_2\)) at 420 cm\(^{-1}\) and the \(\nu_4\) mode at 567 cm\(^{-1}\). Such bands will become more complex in a crystal structure involving more than one cation and degeneracy will be lost. Farmer [28] reports the infrared spectrum of triploidite with formula (Mn,Fe)\(_2\)PO\(_4\)OH with the (\(\nu_1\)) at 957 cm\(^{-1}\), (\(\nu_3\)) at 1090, 1058, 1030 and 1010 cm\(^{-1}\), (\(\nu_2\)) at 420 cm\(^{-1}\) and the \(\nu_4\) mode at 595, 570, 486 cm\(^{-1}\). An hydroxyl stretching frequency of 3509 cm\(^{-1}\) was given. S.D. Ross in Farmer (1974) (page 404) listed some well-known minerals containing phosphate which were either hydrated or hydroxylated or both [28]. The value for the \(\nu_1\) symmetric stretching vibration of PO\(_4\) units was given as 930 cm\(^{-1}\) (augelite), 940 cm\(^{-1}\) (wavellite), 970 cm\(^{-1}\) (rockbridgeite), 995 cm\(^{-1}\) (dufrenite) and 965 cm\(^{-1}\) (beraunite). The position of the symmetric stretching vibration is mineral dependent and a function of the cation and crystal structure. The fact that the symmetric stretching mode is observed in the infrared spectrum affirms a reduction in symmetry of the PO\(_4^{3-}\) units. This reduction in symmetry can be caused by site symmetry and/or factor group splitting.
The Raman spectrum of goyazite over the 100 to 4000 cm\(^{-1}\) range is displayed in Figure 1a. This spectrum shows the overall position of the bands and their relative intensities. It is obvious that there are whole sections of the spectrum where no intensity is observed. This is the reason why the spectra are subdivided into sections based upon the vibrations being studied and a more detailed analysis undertaken. The infrared spectrum over the 500 to 4000 cm\(^{-1}\) region is reported in Figure 1b. In a similar fashion, the infrared spectrum is subdivided into sections for more detailed analysis.

The Raman spectrum in the 800 to 1400 cm\(^{-1}\) region and infrared spectrum in the 500 to 1300 cm\(^{-1}\) region of goyazite are displayed in Figures 2a and 2b respectively. The Raman spectrum of goyazite from Canada is reported in the supplementary information as Figure S1.

The Raman spectrum of goyazite shows a very intense sharp band at 983 cm\(^{-1}\), assigned to the \(\nu_1\) PO\(_4^{3-}\) symmetric stretching mode. In the RRUFF spectrum, a band is observed in the same position (Figure S1). This band is very weak in the infrared spectrum where the band is observed as a shoulder at 981 cm\(^{-1}\). The Raman band observed at 1029 cm\(^{-1}\) with a shoulder at 1037 cm\(^{-1}\) (Figure 2a) and superimposed upon a broad feature at 1087 cm\(^{-1}\) are assigned to the \(\nu_3\) PO\(_4^{3-}\) antisymmetric stretching mode. These bands show much greater intensity in the infrared spectrum (Figure 2b) where intense bands are observed at 1020, 1043 and 1101 cm\(^{-1}\) with shoulders at 1178 and 1209 cm\(^{-1}\). In the RRUFF Raman spectrum an intense band is found at 1032 cm\(^{-1}\). In addition, multiple low intensity bands are observed in the Raman spectrum at 1070, 1096, 1108, 1154, 1186, 1210 and 1235 cm\(^{-1}\). It is suspected that the RRUFF Raman spectrum may contain some minor impurities which contribute to the Raman spectrum; for example some phosphate units may be replaced with carbonate or perhaps sulphate anions. Minerals such as goyazite are often associated with other phosphate minerals including wardite. Further, some cationic substitution can also occur; for example the replacement of Sr by Ba as can occur with the goyazite from Brazil.

Two Raman bands are found at 895 and 927 cm\(^{-1}\). These bands are attributed to the stretching vibrations of the monohydrogen phosphate units. Choi et al. [29] published spectra of NaH\(_2\)PO\(_4\); however these authors did not tabulate or mark the position of the peaks. Therefore, it is very difficult to make any comparison of the peak positions of goyazite and
that of published data by Choi et al. Casciani and Condrate [30] reported bands assigned to these vibrational modes for Ca(H₂PO₄)₂ at 876 and 901 cm⁻¹. In the RRUFF Raman spectrum, three bands are observed at 897, 922 and 932 cm⁻¹. In the Raman spectrum, a broad band is noted at 825 cm⁻¹ and is attributed to the deformation mode of hydroxyl units. This vibration is also observed as a broad band at 831 cm⁻¹ with a shoulder at 794 cm⁻¹ in the infrared spectrum.

The Raman spectrum of goyazite in the 300 to 800 cm⁻¹ and 100 to 300 cm⁻¹ spectral ranges are displayed in Figures 3a and 3b. The series of bands at 556, 581, 596 and 612 cm⁻¹ are assigned to the ν₄ PO₄³⁻ bending modes. In the infrared spectrum (Figure 2b), these phosphate bending modes are noted at 587, 604, 637 and 682 cm⁻¹. In the RRUFF Raman spectrum of goyazite, these bands are found at 556, 585, 609 and 626 cm⁻¹. Two Raman bands (Figure 3b) are observed at 462 and 506 cm⁻¹. These bands are due to the ν₂ PO₄³⁻ in-plane bending modes. In the RRUFF Raman spectrum of goyazite, bands are curve resolved at 451, 461, 508 and 513 cm⁻¹. A very strong Raman band is observed at 367 cm⁻¹ with low intensity shoulder bands at 322 and 338 cm⁻¹. This intense band is attributed to Al-O stretching vibration. Strong Raman bands are recorded in the far low wavenumber region at 187 and 259 cm⁻¹. These bands are simply described as lattice bands. Raman bands are observed in similar positions in the RRUFF spectrum (Figure S3).

The Raman spectrum of goyazite in the OH stretching region is reported in Figure 4a. The infrared spectrum of the OH stretching region is illustrated in Figure 4b. Two sharp bands are noted at 3609 and 3631 cm⁻¹. These bands are attributed to OH stretching vibrations from the hydroxyl units. Broad Raman bands are observed at 2924, 3043, 3210, 3429 and 3511 cm⁻¹ and are assigned to water stretching vibrations. A remarkably similar spectrum is observed in the infrared spectrum of this spectral range. Infrared bands are curve resolved at 3082, 3173, 3381, 3423 and 3493 cm⁻¹. These bands are assigned to water stretching vibrations. The observation of multiple water bands suggests that not all the water molecules are equivalent in the structure of goyazite. Further, the position of the water bands shows that water is involved in the structure with different hydrogen bond strengths. The lower the position of the water stretching vibration, the stronger the hydrogen bond as measured by the shorter hydrogen bond distances.
Conclusions

Raman spectroscopy complimented with infrared spectroscopy has been used to study the molecular structure of the mineral goyazite. Goyazite is a member of the crandallite subgroup of the alunite supergroup. The crystal structure is of the alunite-type and consists of sheets of corner-sharing AlO$_6$ octahedra parallel to (0001). The octahedrally coordinated Sr$^{2+}$ cations occupy cavities between pairs of octahedral sheets and are surrounded by six oxygen atoms from the ($\text{Al}^{3+}$)O$_6$ octahedra. Considerable variation is observed between the spectra of goyazite mineral samples from different origins.

Raman spectroscopy based upon the observation of a single symmetric phosphate stretching mode, shows that there is only one equivalent type of phosphate unit in the goyazite structure. However, the observation of bands attributed to hydrogen phosphate units shows that these moieties are also in the structure of goyazite. Raman bands at 3609 and 3631 cm$^{-1}$ are attributed to OH stretching vibrations from the goyazite hydroxyl units. The observation of broad Raman bands at 2924, 3043, 3210, 3429 and 3511 cm$^{-1}$ attributed to water stretching vibrations supports the concept that the water molecules in the goyazite structure are not equivalent. This results in a range of hydrogen bond distances for water in the goyazite structure.

Acknowledgments

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REFERENCES

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