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Comparison of the Raman spectra of Bayerite, Boehmite, Diaspore and Gibbsite

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ABSTRACT

Gibbsite and bayerite are alumina trihydrate ($\text{Al}(\text{OH})_3$). Gibbsite occurs abundantly in nature, usually as a major mineral component in bauxite whereas bayerite is rarely found in nature. Boehmite and diaspore are alumina oxhydroxide (AlOOH) and are two other important minerals in bauxite. The Raman spectra of these four minerals were obtained using a Fourier transform Raman spectrometer operating at 1064 nm. Bayerite spectrum shows five absorption bands, 3652, 3542, 3449, 3438, and 3421 cm^{-1} and the gibbsite spectrum shows four strong and sharp absorption bands, 3619, 3523, 3433 and 3363 cm^{-1} in the hydroxyl stretching region. Four broad bands, 3426, 3365, 3229 and 2935 cm^{-1} and three weak bands, 3420, 3216 and 3090 cm^{-1} are present in this region for diaspore and boehmite, respectively. The Raman bands correspond well with the infrared absorption bands at 3620, 3525 cm^{-1} for gibbsite, 3365 cm^{-1} for diaspore and 3423, 3096 cm^{-1} for boehmite and these bands are assigned to be Raman and infrared active. The spectra of bayerite, gibbsite and diaspore are complex while the spectrum of boehmite only illustrates four absorption bands in the low frequency region. Common bands of RT-Raman spectra at 1019, 892, 816, 710, 568, 539, 506, 429, 395, 379, 321, 306, 255 and 242 cm^{-1} were observed for gibbsite, 1079, 1068, 898, 866, 545, 434, 388, 322, 292, 250 and 239 cm^{-1} for bayerite, 705, 608, 446, 260 and 216 cm^{-1} for diaspore, and 674, 495 and 360 cm^{-1} for boehmite. The differences in the vibrational spectra of bayerite, gibbsite, diaspore and boehmite are interpreted as being due to the differences in the molecular structure of these minerals.

INTRODUCTION

Gibbsite [$\gamma\text{-Al}(\text{OH})_3$], Boehmite ($\gamma\text{-AlOOH}$) and Diaspore ($\alpha\text{-AlOOH}$) are the three principal hydrates of aluminum and are found in lateritic or terra rossa soils and various sediments. Bayerite [$\alpha\text{-Al}(\text{OH})_3$] is a monocline mineral and is in a meta-stable stage. It is an intermediate product between amorphous $\text{Al}(\text{OH})_3 \cdot n\text{H}_2\text{O}$ (cliachite, alumogel) and monocline gibbsite or hydrargillite^[1]. Bayerite is very rare in nature but can be easily synthesised in the laboratory^[2].

Gibbsite, boehmite and diaspore form the main constituents of bauxite and laterites, with gibbsite often being the predominant mineral^[3] and diaspore being the minor constituent in many bauxites in addition to gibbsite and boehmite^[1, 4, 5]. Bauxite deposits provide industry with raw materials as the major source of aluminium. Bauxite deposits occur in hot rainy climates that have and a dry period such as monsoon^[1]. In Australia large deposits are mostly found in subtropical regions with Weipa in North Queensland being one of the major deposit sites. Weipa bauxites contain about 70% gibbsite and 30% boehmite. Kaolinite, allophane, quartz, goethite and hematite are commonly associated with bauxite as impurities.

The gibbsite and bayerite are bound by the same structural sheetlike unit, which consists of a layer of aluminium ions sandwiched between two layers of hexagonally

packed hydroxyl ions, in the plane defined by the *a* and *b* axes. The oxygens of one layer lie directly above the oxygens at the top of the layer below. The sheetlike units are stacked along the axis^[3, 6, 7]. The difference in structure between gibbsite and bayerite is that one can be generated from the other by a rotation about the *c* axis of one of the sheetlike units by 60°^[7]. The structure of boehmite consists of double layers of oxygen octahedra partially filled with Al cations. The stacking arrangement of the three oxygen layers is such that the double octahedral layer is in cubic closed packing^[8, 9]. Boehmite is isostructural with lepidocrocite (γ -FeOOH). The structure of diaspoire is based on layers of oxygen atoms in hexagonal close packing; the isostructure of diaspoire is goethite (α -FeOOH)^[10-13]. Diaspoire and boehmite are polymorphs of the same mineral and differ in structural relationships by the packing of the oxygens.

Vibrational spectroscopy has been extensively applied to characterise the phases of the Al₂O₃-H₂O system over a long period of time and previous work relied mainly on infrared spectroscopic investigation^[14]. Huneke et al.^[2] recommended Raman as an advanced technique over X-ray diffraction in the study of the mixture of gibbsite and bayerite. By combining the Raman and infrared spectra, Kiss et al.^[15] have well determined the structure of boehmite. The most recent work of Frost et al.^[3, 8, 10] has contributed to an understanding of the structural vibration of these aluminium oxohydroxides and have paved the way in using infrared and Raman techniques for mineral characterisation and phase transformation. In this paper we report the investigation of gibbsite, bayerite, boehmite and diaspoire based on FT-Raman spectroscopy and the comparison of Raman spectra with these four minerals in characterization of different aluminium phases. Manipulation of band components is depended mainly on the vibration of structural and surface hydroxyl groups.

MATERIALS AND METHODS

The gibbsite, bayerite and boehmite were synthesized from aluminium salt and the details of these minerals was fully described elsewhere^[3, 8, 10]. Diaspoire was a natural sample from Nevada of the USA.

FT-Raman spectra of gibbsite, bayerite, boehmite and diaspoire were obtained using the Perki-Elmer 2000 series Fourier Transform spectrometer fitted with a Raman accessory comprising of a Spectron Laser Systems SL301 Nd-YAG laser operating at a wavelength of 1064 nm, and Raman sampling compartment incorporation 180 degree optics. Raman shifts were observed in the spectral range 4000-200 cm⁻¹. Single beam spectra were corrected for instrument function and detector response. Raman spectra were obtained directly by using a sample of the raw mineral directly in the incident beam at a resolution of 4 cm⁻¹. Measurement times between 0.3 and 1.5 hours with 32 to 256 scans were used to collect spectra. A laser power of 200 mV was used so that this power is low enough to prevent damage to the samples but is sufficient to produce good quality spectra in a reasonable time.

Manipulation of spectra including baseline adjustment, smoothing, normalization and spectrum correction was performed with the use of the GRAMS software package (Galactic Industries Corporation). Band component analysis was undertaken with the Jandel "Peakfit" software package, which enables the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was carried out 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 0.990.

RESULTS AND DISCUSSION

The bands of Raman spectra of gibbsite, bayerite, diaspore and boehmite are mainly assigned in the low frequency region between 200 and 1200 cm^{-1} (Fig. 1a) and the hydroxyl stretching region between 2800 and 3700 cm^{-1} (Fig. 1b). The band positions of the Raman shift of the hydroxyl stretching, hydroxyl bending and hydroxyl deformations are shown in Table 1. The hydroxyl stretching region is characteristic of the $\nu(\text{OH})$ stretching mode of the hydroxide^[2, 3, 8, 10, 14, 16]. The low frequency region consists of $\delta(\text{OH})$ and $\gamma(\text{OH})$ modes (Table 1), which involve AlOH deformation and Al-O-Al skeletal flexing vibrations.

Gibbsite

The gibbsite spectrum shows four strong and sharp absorption bands at 3617, 3522, 3433 and 3364 cm^{-1} at the hydroxyl stretching region (Fig. 2a). Our result is identical to that of Huneke et al.^[2] who observed four strong bands at 3615, 3520, 3431 and 3361 cm^{-1} . Frost et al.^[3] observed three strong bands at 3524, 3436 and 3365 cm^{-1} of FT-Raman, five bands at 3620, 3524, 3452, 3395 and 3375 cm^{-1} of infrared absorption and four bands at 3617, 3532, 3489 and 3351 cm^{-1} of infrared emission. Farmer^[14] (1974) reported that synthetic polycrystalline gibbsite showed infrared absorption bands at 3617, 3520, 3428 and 3380 cm^{-1} after his extensive studies on the phases of the $\text{Al}_2\text{O}_3\text{-H}_2\text{O}$ system over a long period of time.

It has been reported that the infrared absorption band at 3460 cm^{-1} is polarized perpendicular to the 001 plane and the bands at 3617 and 3522 cm^{-1} are polarized in this plane, which is parallel to the $\text{Al}(\text{OH})_3$ layer in the gibbsite structure^[3, 17]. All bands of Raman spectra in the hydroxyl stretching region are assigned as $\nu(\text{OH})$. It is suggested that the bands at 3364 cm^{-1} is associated with hydrogen bonds between the layers, whereas the two higher frequency bands correspond to longer hydrogen bonds between hydroxyls lying in the same plane. A higher frequency band is considered to be associated with a longer hydrogen bond distance.

Because gibbsite bands of Raman spectra at 3617, 3522, 3433 and 3364 cm^{-1} correspond well with the bands of infrared spectra at 3617, 3520, 3428 and 3380 cm^{-1} , these bands are both Raman and infrared active. This finding is consistent with that of Mardilovich and Trokhimets^[18] and Huneke et al.^[2]. However, the 3617 cm^{-1} band has been reported as a Raman inactive band although it is expected to be an active one^[3] as this band is readily observed in the Raman spectra of kaolinite, which contains a gibbsite and a siloxane sheet linked through an apical oxygen^[19, 20]. This may be due to a better polarizability of hydroxyl stretching frequencies for the present sample than for those reported in previous work.

The hydroxyl deformation models are observed at 1051, 1019, 980 and 916 cm^{-1} , which correspond to that of the infrared investigation at 1060, 1024 and 969 and 914 cm^{-1} ^[3]. Our observation is also identical to Raman results of natural samples used by Huneke et al.^[2] although their results showed poor resolution at 1051, 980 and 916 cm^{-1} bands. These four hydroxyl deformation models at 1051, 1019, 980 and 916 cm^{-1} seem to correspond to 3617, 3522, 3433 and 3364 cm^{-1} bands in the hydroxyl stretching region.

The band at around 916 cm^{-1} is ascribed to an Al(OH)Al group free from hydrogen bonding and is commonly assigned to the hydroxyl deformation vibration of aluminium oxohydroxides^[19-22]. Kolesova and Ryskin^[23] found that the 1020 , 958 and 916 cm^{-1} bands disappeared in the infrared spectrum of Al(OD)₃ compared with that of Al(OH)₃ and confirmed that these bands were assigned to the vibrations of hydroxyl groups. They assumed that the 1021 cm^{-1} band is evoked by bending $\delta(\text{OH})$ vibrations of the hydroxyl groups associated under the influence of the hydrogen bond, while the 958 and 916 cm^{-1} bands are evoked by $\delta(\text{OH})$ vibrations of weakly interacting hydroxyl groups.

Major bands in the low frequency Raman spectrum of gibbsite are found at 892 , 816 , 710 , 568 , 539 , 506 , 429 , 395 , 375 , 321 , 306 , 255 and 242 cm^{-1} . Weak bands are also found at 842 , 788 , 753 , 620 , 604 , 444 , 412 , 372 , 290 and 263 cm^{-1} . The bands with most intensity are at 568 , 539 and 321 cm^{-1} . The 568 and 539 cm^{-1} bands are attributed to Al-O-Al deformation while the 321 cm^{-1} band with a shoulder at 307 cm^{-1} is ascribed to Al-O-Al stretching vibrations.

Bayerite

The bayerite spectrum shows seven absorption bands at 3664 , 3652 , 3552 , 3542 , 3450 , 3438 and 3420 cm^{-1} (Fig. 2b) and is distinct from that of gibbsite in the hydroxyl stretching region. The three major bands at 3652 , 3542 and 3420 cm^{-1} are identical to those found by Huneke et al.^[2] at 3651 , 3542 and 3421 cm^{-1} . As mentioned above, bayerite consists of the same hexagonally packed hydroxyl group as does gibbsite. The crystal structure of both minerals is monoclinic, $P2_1/n$, with $a = 5.0626\text{ \AA}$, $b = 8.6719\text{ \AA}$, $c = 9.4254\text{ \AA}$, $\beta = 90.26^\circ$ and $z = 4$ for bayerite and $a = 8.684\text{ \AA}$, $b = 5.078\text{ \AA}$, $c = 9.736\text{ \AA}$, $\beta = 94.54^\circ$ and $z = 8$ gibbsite^[24]. Differences in the Raman spectra in the stretching vibration region may reflect the Al-OH distance compared 1.74 - 2.06 \AA of bayerite with 1.73 - 2.14 \AA of gibbsite and the OH-OH distance of 2.92 - 3.24 \AA of bayerite with 2.75 - 3.24 \AA of gibbsite^[14]. Three shoulder peaks at 3552 , 3450 and 3438 cm^{-1} may be attributed to surface hydroxyl group in the bayerite structure.

The bayerite spectrum in the low frequency region is not as complex as is gibbsite and these two phases are therefore well distinguished although bands at 898 , 443 , 322 cm^{-1} may overlap with the gibbsite bands at 892 , 444 and 321 cm^{-1} . However, other bands at 1079 , 1068 , 866 , 545 , 525 , 484 , 434 , 388 , 359 , 297 , 250 , 239 and 205 are well resolved and are distinctly different from those of gibbsite. FT-Raman spectroscopy is considered to be a precise and fast technique in characterizing minerals that have similar atomic close packing.

Diaspore

Five broad bands at 3445 , 3363 , 3226 , 3119 and 2936 cm^{-1} (Fig. 2c) are observed for diaspore in the hydroxyl stretching region. These bands are well manipulated using the peak fit technique as illustrated in Fig. 2c. Infrared investigation on diaspore has shown differences in band position. Farmer^[14] reported two bands at 2994 and 2915 cm^{-1} , which are similar to 2985 and 2910 cm^{-1} obtained by van der Marel and Beutelspacher^[1] but differed from 3365 , 3284 , 3095 and 2938 cm^{-1} observed by Frost et al.^[10]. The differences may be due to the variation of distribution of surface hydroxyl groups in natural samples used in their studies apart from manipulation technique. Band overlap is obviously in natural diaspore used in this study and band components are only resolved through band component analysis. By comparing our

results with that of Frost et al.^[10] the 3363 and 2936 cm^{-1} bands are both Raman and infrared active.

Broad and weak bands at 1186, 1065, 1045 and 956 cm^{-1} are assigned to the Al(OH) bending models of diaspore. Bands at 705, 446 and 260 cm^{-1} are the most intense in the Raman spectrum and bands at 917, 838, 812, 790, 664, 608, 581, 551, 496, 394, 365, 328, 287, and 208 cm^{-1} are much weaker. The 705, 446 and 260 cm^{-1} bands are assigned to the symmetric stretching modes, the 260 cm^{-1} to Al-O-Al symmetric stretch and the 446 cm^{-1} band to the Al-O-Al bend.

Boehmite

Four weak and broad bands at 3371, 3220, 3085 and 2989 cm^{-1} are the distinguishing features for boehmite (Fig. 2d). Two broad bands at 3371 and 2989 cm^{-1} are probably due to surface hydroxyl groups. This type of hydroxyl group is easily formed during the synthesis of boehmite. Similarly two broad bands at 3237 and 3423 cm^{-1} of Raman spectra of pure water has been observed. The shift of these two bands to lower positions seems to be attributed to the effect of Al-OH bonding. Previous work on near infrared FT-Raman has confirmed that a broad background is due to surface hydroxyl groups^[25]. Frost et al.^[8, 10] who characterized hydroxyl stretching bands at 3413, 3283, 3096 and 2997 cm^{-1} have also discovered broad backgrounds. Recent work on FT-infrared spectroscopy further confirmed that a shoulder band at 3494 cm^{-1} and a broad band at 1640 cm^{-1} were assigned to the stretching and bending modes of adsorbed water in addition to two distinct $\nu(\text{OH})$ stretching modes at 3292 and 3097 cm^{-1} ^[26]. The 3085 and 2989 cm^{-1} bands of Raman spectra correspond well to the 3096 and 2997 cm^{-1} of infrared absorption bands. The bands at 3220 and 3085 cm^{-1} may be attributed to the hydroxyl stretching frequencies of the hydroxyl group within the structure.

The low frequency region (200-1200 cm^{-1}) of boehmite consists of hydroxyl deformation modes (900-1050 cm^{-1}) and hydroxyl translation modes (400-800 cm^{-1}). Three very strong bands are observed at 674, 495 and 360 cm^{-1} associated with very weak bands at 1080, 1057, 730 and 450 cm^{-1} . The two hydroxyl deformation bands at 1080 and 1057 cm^{-1} are similar to those at 1091 and 1049 cm^{-1} of FT-Raman shift but differ from the 1071 and 1161 bands of infrared absorption reported in previous work^[8].

CONCLUSIONS

Raman spectra presented in this study are distinctly different in gibbsite, bayerite, diaspore and boehmite. Characterization depends particularly on the vibrations of structural and surface hydroxyl groups. In aluminium oxohydroxides lower frequencies in the hydroxyl stretching region between 2800 and 3700 cm^{-1} correspond to the smaller distances between the oxygen atoms of the hydroxyl groups. Vibrational spectra in the range between 700 and 2000 cm^{-1} can be considered as evidence of the considerable portion of covalency of the Al-O bond in the AlOH system. A comparison of band component analyses for gibbsite, bayerite, diaspore and boehmite indicates that assignment is dependent on the different molecular structures. FT-Raman spectroscopy is thus considered to be a fast, non-destructive technique for pure and mixed phase characterization, and has the unique advantage in using raw samples without structural disturbance. Another advantage of FT-Raman spectroscopy is the

ability to make measurement to 50 cm^{-1} compared to 400 cm^{-1} with infrared spectroscopy.

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