High-Pressure Raman Study on Anglesite*

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ABSTRACT

High-pressure Raman spectroscopic experiments of anglesite, PbSO₄, were carried out in a diamond anvil cell up to about 35 GPa at room temperature. Two stages of changes in the pattern of wavenumber-versus-pressure plot were observed in most of the vibrational modes. The first stage of change is the kink in the slope of wavenumber-versus-pressure plot at about 14 GPa, indicating a change in the force constant of modes. Further compression up to 21 GPa causes the splitting in the S-O stretching modes, representing the distortion of SO₄ tetrahedron. The behavior of transition observed in PbSO₄ is similar to that of BaSO₄ as well as those found in the solid solution series of BaSO₄-SrSO₄. Transitions taking place at higher pressure for anglesite is due to the relatively greater value of electronegativity for Pb²⁺, as compared with M²⁺ in other complex compounds of similar structure.

Keywords: Anglesite; High-Pressure; Raman Spectroscopy; Electronegativity

1. Introduction

High-pressure research in Earth sciences has been focused on silicate minerals that are directly relevant to the Earth’s interior and much less attention has been paid to other rock-forming minerals. However, recent investigations on some sulfates [1-3] and hydroxides [4,5] had provided interesting observations for the understanding of the behaviors of OH groups in hydrous minerals as well as the structural changes on sulfates under high-pressure. High-pressure study on sulfates is important because sulfates have analogous structure as olivine but with much greater compressibility. It is comprehensible that high-pressure study on the distortion of SO₄ tetrahedron and the lattice stability of sulfates may have direct implications on the seemingly stiffer iso-structural silicates.

The minerals with a structure of barite-type, such as barite (BaSO₄), anglesite (PbSO₄), and celestite (SrSO₄), are some of the most widely distributed sulfates in the world. The structure of barite was reported as orthorhombic system with space group Pbnm [6]. In our previous investigation, we found that BaSO₄ shows anisotropic compressibility along three crystallographic axes with c being the most compressible axis [2]. A phase transformation at 10 GPa for barite was also reported [3]. Anglesite, PbSO₄, has the same structure as barite and forms complete solid solution with barite in the BaSO₄-PbSO₄ series [7,8]. Previous investigation on another Ba-related solid solution, BaSO₄-SrSO₄ series, reveals that similar phase transitions occur in members of this series and the pressures at which transitions take place increases with the decrease in the size of M²⁺ cations [9,10]. Since the two M²⁺ cations, Ba²⁺ and Pb²⁺, have very different chemical and physical behaviors, such as electronegativity and electron configuration etc., it is interesting to conduct high-pressure investigation on anglesite for the understanding of the effect of the cation exchange in the lattice dynamics of the analogous BaSO₄ structure.

2. Experimental Methods

Raman scattering method was applied to the study of the behaviors of anglesite at high-pressure. The experimental details are described as follows. Crystals of synthetic anglesite [11] were ground to fine powder and used as the starting material. The sample was first examined by the Raman spectroscopy for its identity [12]. A disk of T301 stainless steel with an original thickness of 250 μm was used as gasket in the high-pressure work. The gasket was compressed between the diamond anvils to make an indentation on which a hole of 150 μm was drilled for the sample chamber. After the chamber was loaded with sample, it was then filled with a 4:1 methanol-ethanol mixture as a pressure-transmit-
ting medium and then gradually compressed to high-pressure. Ruby fluorescence method was used for pressure measurement [13] after each pressure increments. In each pressure measurement, we measured more than three ruby grains to estimate the pressure distribution of the compressed sample.

A Renishaw 2000 type spectroscopy was used in the Raman spectroscopic study. An Ar-ion laser beam (514.5 nm) was used as an excitation source. The laser light (about 5 µm in diameter) was focused on the sample in the diamond cell and back-scattered Raman signals were collected by the CCD (charge-coupled device) detector. The power for the laser source used was 100 to 500 mW and recording time for each Raman spectrum was 20 to 60 seconds. Pressure was recorded before and after each Raman spectrum was collected. Both loading and unloading processes were conducted. The uncertainties in pressure and wavenumber readings are 0.5 GPa and 1 cm\(^{-1}\), respectively.

3. Results

Some of the representative Raman spectra of anglesite taken during the loading and unloading processes of the experiment are shown in Figure 1. The Raman \(\nu_1\) (non-degenerate symmetric stretching mode at 978 cm\(^{-1}\)), \(\nu_2\) (doubly degenerate symmetric bending mode at 439, 450 cm\(^{-1}\)), \(\nu_3\) (triply degenerate asymmetric stretching mode at 1064, 1157 cm\(^{-1}\)) and \(\nu_4\) (triply degenerate asymmetric bending mode at 606, 616, 642 cm\(^{-1}\)) of anglesite are observed at the ambient conditions in this study. This is in excellent agreement with that reported in the literature. [10,11] Griffith [12] reported that anglesite exhibited more than nine relatively intense Raman bands at the ambient conditions (\(\nu_3\) mode (1057, 1068, 1162 cm\(^{-1}\))). However, several Raman modes are not observed in this measurement. The reason for this is probably due to a considerable mixing of the translational and rotational bands which were not easily resolved in the anglesite crystal [14].

The frequencies of Raman modes are found to increase, but their intensity becomes weaker with increasing pressure. Most Raman bands of anglesite remain quite sharp at all pressures. It is found that the \(\nu_1\) mode splits into two recognizable peaks when the pressure exceeds 21 GPa, and the intensity of the new peak becomes stronger with increasing pressure. The \(\nu_{3b}\) mode also splits into two peaks when the pressure exceeds 21 GPa, but it is too weak to be defined. No sign of splitting is detected for the \(\nu_2\) and \(\nu_4\) mode throughout the entire pressure range up to 35 GPa.

The variations of the frequency with respect to pressure for all the observable Raman bands of anglesite are plotted in Figure 2. Interesting phenomena are observed as well as the splitting of stretching modes of S-O. In Figure 2, it is noted that all Raman bands are seen to vary linearly with pressure up to about 14 GPa. With further compression, apparent kinks or discontinuities in the wavenumber-versus-pressure plot are detected for almost all modes.

The changes in the slope (\(d\nu/dP\)) of each Raman mode of anglesite with pressure are listed in Table 1. The \(\nu_1\) mode is the most intense Raman mode of anglesite. The anglesite phase was recovered during the unloading process.

![Figure 1](image-url)  
**Figure 1.** A series of Raman spectra of anglesite shows the effect of pressure on the four Raman modes. The \(\nu_1\) mode is the most intense Raman mode of anglesite. The anglesite phase was recovered during the unloading process.
Figure 2. A plot shows the shifts of the wavenumber of each Raman mode of anglesite as a function of pressure. Data for loading process are shown as solid symbols and those for unloading process as open symbols. Two stages of change in the slope of each mode as well as the change in the number of modes can be observed. The “kink” at which a discontinuity in the slope of wavenumber vs. pressure plot is seen for each mode at 14 GPa. The solid lines are the eyeball linear fit of the data (note the difference in the scale on the vertical-axis of the pattern).

Table 1. The variations of the slope (dv/dP, cm\(^{-1}\)/GPa) of each Raman mode in anglesite.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Slope (R(^2))</th>
<th>Pressure (GPa)</th>
<th>14</th>
<th>21</th>
</tr>
</thead>
<tbody>
<tr>
<td>(v_1)</td>
<td>4.00 (0.997)</td>
<td>3.53 (0.978)</td>
<td>3.18 (0.992)</td>
<td></td>
</tr>
<tr>
<td>(v_2)</td>
<td>2.26 (0.995)</td>
<td>1.88 (0.909)</td>
<td>1.59 (0.990)</td>
<td></td>
</tr>
<tr>
<td>(v_3)</td>
<td>2.53 (0.991)</td>
<td>2.15 (0.771)</td>
<td>2.10 (0.990)</td>
<td></td>
</tr>
<tr>
<td>(v_4)</td>
<td>3.83 (0.964)</td>
<td>3.55 (0.805)</td>
<td>3.09 (0.990)</td>
<td></td>
</tr>
<tr>
<td>(v_5)</td>
<td>3.52 (0.993)</td>
<td>2.47 (0.999)</td>
<td>2.23 (0.915)</td>
<td></td>
</tr>
<tr>
<td>(v_6)</td>
<td>0.55 (0.775)</td>
<td>0.89 (0.821)</td>
<td>1.33 (0.950)</td>
<td></td>
</tr>
<tr>
<td>(v_7)</td>
<td>1.45 (0.896)</td>
<td>1.48 (0.974)</td>
<td>1.00 (0.952)</td>
<td></td>
</tr>
<tr>
<td>(v_8)</td>
<td>1.73 (0.998)</td>
<td>1.63 (0.822)</td>
<td>1.56 (0.984)</td>
<td></td>
</tr>
</tbody>
</table>

4. Discussion

In the structure of anglesite, each sulfur atom is surrounded by four oxygen atoms and forms an SO\(_4\) tetrahedron while each lead atom coordinates with 12 oxygens. Among the 12 oxygen atoms, 11 atoms shared with the nearest six neighboring SO\(_4\) tetrahedra and the twelfth oxygen associates with another SO\(_4\) tetrahedron. In other words, each Pb\(^{2+}\) is coordinated with 12 oxygen ions to form seven different SO\(_4\) groups [6]. The Raman modes observed in this study are all assigned to the stretching and bending of the S-O modes. These S-O modes are nevertheless affected by the relative changes of Pb-O distance during the compression process. When anglesite is compressed, the change in the bond distance between Pb-O would respond more to the compression force than that between S-O in the SO\(_4\) tetrahedron due to the fact that PbO\(_{12}\) polyhedra are more compressible than SO\(_4\) tetrahedron. Therefore, the bonding distances between Pb and O tend to decrease more than those between S and O during initial stage of compression process. However, when PbO\(_{12}\) polyhedra are compressed further, the Pb-O distances gradually decrease and their bonding strengths increase in the meantime. As a consequence, the force constants of various band of S-O in SO\(_4\) tetrahedra will also change since their bonding oxygens are sharing with Pb in PbO\(_{12}\) polyhedra. The discontinuity in the slope dv/dP for various Raman modes at 14 GPa signifies that the PbO\(_{12}\) polyhedra are compressed to the extend that their average Pb-O distance reaches a critical state as to cause a sudden change in the bonding forces of various S-O bonds. The change in the force constant among various S-O bands in SO\(_4\) tetrahedra result in the deviation of compression data from the normal compression curve above 14 GPa.
Although there are changes in the force constant in various S-O bonds, the SO₄ tetrahedra in the lattice remain undistorted until they are compressed up to 21 GPa where additional modes appear in the stretching bands (Figure 2), accompanying the slight but noticeable change in the slope of all S-O modes (Table 1). These phenomena are attributed to the distortion of SO₄ tetrahedra as their bonding oxygens are further bonded with Pb of PbO₁₂ polyhedra as more and more pressure is applied. The distortion of SO₄ tetrahedra persists up to 35 GPa in this experiment. The distortion of SO₄ tetrahedra as well as the change in the force constants of various S-O bonds is, nevertheless, reversible that the wavenumbers of all vibration modes follow the trend of compression process during the unloading process.

Barite, celestite and anglesite all have the same structure with different M²⁺ cations (Table 2). It is interesting to note that similar changes in the vibrational modes are observed among these compounds under high-pressure [3, 9; also see Table 2]. The variations of the frequency with respect to pressure for Raman v₁ mode of barite, celestite and anglesite are plotted in Figure 3. From Figure 3, we know the pressures at which the kinks in slope as well as the split of SO₄ tetrahedra take place are different in those minerals. The pressure at which the first kink takes place is 8, 10 and 14 GPa for barite, celestite and anglesite, respectively. The pressure at which the second kink takes place is 17, 18 and 21 GPa for barite, celestite and anglesite, respectively.

As we noted in Table 2 that these compounds have similar M-O bonding lengths and S-O bonding force constants and, therefore, it is not surprising that they behave similarly under high pressure. Chen et al. [10] reported that 2 stages of changes in Raman modes occur at high pressure in the BaSO₄-SrSO₄ solid solution series. The compound with larger cation tends to undergo structural modifications at a pressure lower than that with smaller cation. Since the size of Ba²⁺ is larger than Sr²⁺ and Pb²⁺, the transitions take place in BaSO₄ are at pressures lower than those in SrSO₄ and PbSO₄. However, the fact that the pressures at which transitions occur in SrSO₄ are lower than those in PbSO₄ is not accounted for by the effect of cation size since the size of Pb²⁺ is larger than Sr²⁺ that the transitions in PbSO₄ should be expected to take place at pressures lower than those in SrSO₄. Apparently, factors that cause the transitions in PbSO₄ at pressures higher than those in SrSO₄ other than the difference in size are needed.

Miyake et al. [15] reported that the electronegativity of a metal and the Coulombic force between cation and oxygen may modify the symmetry of the SO₄ tetrahedron. For instance, the cation-oxygen bonding length in PbSO₄ is shorter than BaSO₄ due to their difference in electronegativity of M²⁺. Though the size of Pb²⁺ is smaller than that of Sr²⁺, the electronegativity of Pb²⁺ is much larger than Sr²⁺ (Table 2). Higher value in electronegativity for a cation implies that it tends to form stronger bond with anions such as oxygen. Therefore, the bonding force of Pb-O in PbO₁₂ polyhedra is higher than that of Sr-O in SrO₁₂ polyhedra at the ambient conditions. The PbO₁₂ polyhedra in PbSO₄ are more difficult to compress and the effect on the changes of force constants in S-O bonds would be expected to occur at pressure much higher than those in SrSO₄. That explains why the kinks and splitting in SO₄ stretching modes in PbSO₄ take place at pressure higher than those in SrSO₄.

### 5. Conclusion

Raman spectroscopic observation on PbSO₄ at high-pressure up to 35 GPa shows two stages of changes in the pattern of wavenumber-versus-pressure plot in most of the vibrational modes. The first stage of change is the kink in the slope of wavenumber-versus-pressure plot at about 14 GPa, indicating a change in the force constant of modes. Further compression up to 21 GPa causes the splitting in the S-O stretching modes, representing the distortion of SO₄ tetrahedron. Similar changes of Raman modes in PbSO₄ are present in members of the solid solution series of BaSO₄-SrSO₄. Transitions taking place at

| Table 2. Some characterized parameters of barite, celestite and anglesite. |
|------------------|------------------|------------------|------------------|
| M = Ba, Sr or Pb | Barite (BaSO₄)   | Celestite (SrSO₄)| Anglesite (PbSO₄)|
| M-O bond length (Average M-O length) (Å) | 2.951*           | 2.827*           | 2.864*           |
| S-O Bonding force constants (H, md/Å)³ | 2.952*           | 2.831*           | 2.870*           |
| S-O Stretching force constants (K, md/Å)⁵ | 0.46             | 0.47             | 0.42             |
| M²⁺ radius (Å) | 6.27             | 6.34             | 5.98             |
| Electronegativity of M²⁺ | 1.6              | 1.44             | 1.49             |
| Pressure of Raman v₁ mode slope change | 0.9              | 1.0              | 1.8              |
| 1st | 8 | 10 | 14 |  |
| 2nd | 17 | 18 | 21 |  |

*Jacobsen et al. (1998) [16]. *Miyake et al. (1978) [15].
higher pressure for PbSO$_4$ is due to the relatively greater value of electronegativity for Pb$^{2+}$, as compared with M$^{2+}$ in other complex compounds of similar structure.

REFERENCES


