

# Crystal structure and Raman spectral studies of BaSO<sub>4</sub>–PbSO<sub>4</sub> solid solution

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Received October 4, 2002; resubmitted July 26, 2004; accepted September 10, 2004

*Hokutolite / Solid solution / Raman spectroscopy /  
Single crystal structure analysis / X-ray diffraction*

**Abstract.** Natural hokutolite, (Ba,Pb)SO<sub>4</sub>, is a radioactive sulfate mineral occurring in hot-spring deposit. Unlike the limited PbSO<sub>4</sub> content observed in natural specimens, the present study reveals that (Ba,Pb)SO<sub>4</sub> crystals can be grown with compositions covering the whole solid solution series of PbSO<sub>4</sub> and BaSO<sub>4</sub>. X-ray measurements show that the unit cell parameters gradually increase with increasing BaSO<sub>4</sub> content. The nonlinear behavior of the unit cell dimensions with composition shows that a positive deviation from linear variation exists in the *b*-axis direction and negative deviations for *a*- and *c*-axes. It is evident that the variations in the *M*-O bond lengths result in the significantly negative deviations of all unit cell parameters from Vegard's rule around 70 mol% BaSO<sub>4</sub>. Hence, the abnormally negative deviations of all unit cell parameters from Vegard's rule are primarily attributed to the discontinuities in the mean *M*-O bond lengths. In addition, the existence of structure gap in natural hokutolite samples reported may be ascribed to the same reason.

Raman bands in these synthetic crystals show monotonous changes in  $\nu_1$  frequency from anglesite to barite. It is inferred that the slight decrease in  $\nu_1$  frequency for crystals with BaSO<sub>4</sub> content being smaller than 20 mol% may be attributed to the net effect of the S–O force constants, intertetrahedral O–O force constants, and distortions of SO<sub>4</sub> tetrahedra. The present results also indicate that the positional disordering along the solid solution series is responsible for the Raman line broadening, showing the local maximum in the line width plot occurs at about 50 mol% substitution. This work also demonstrates that variations of Raman shift of  $\nu_1$  band as well as its line width are essentially related to the random Pb–Ba substitution in our synthetic crystals.

## Introduction

Hokutolite, a Pb-bearing barium sulfate, is a radioactive mineral and was first discovered at Peitou, Taiwan by Okamoto (Chang, 1961) in 1907. There has been some questions whether or not a perfect solid solution of the system BaSO<sub>4</sub>–PbSO<sub>4</sub> is formed in the whole range of composition. Moreover, Takano (1959) studied naturally occurring lead-bearing barite (hokutolite) by X-ray and showed that this system did not obey Vegard's rule. Apart from the above conclusion, Takiyama (1967) reported that, on the basis of X-ray powder patterns and electron microscopic data, the precipitates formed at room temperature with the solutions of barium chloride, lead nitrate and ammonium sulfate as starting materials were single phases with their lattice parameters obeying Vegard's rule. Sugitani et al. (1969) carried out a more detailed examination on this system by X-ray powder diffraction studies and reached the same conclusion as Takiyama's. Boström et al. (1967) investigated the solid solutions of the BaSO<sub>4</sub>–PbSO<sub>4</sub> system at 100, 300 and 375 °C. They concluded that the unit cell dimensions of the solid solutions showed monotonous variations with the ratios of BaSO<sub>4</sub>/PbSO<sub>4</sub>. However, a structural gap found in the natural lead-bearing barite (Takano, 1959) was observed indirectly on the precipitated BaSO<sub>4</sub>–PbSO<sub>4</sub> solid solutions on the basis of some measurements by Takano et al. (1969). They indicated that the structural gap exists at the composition of 25% and possibly 75 mol% of PbSO<sub>4</sub> on the basis of their measurements.

Based on the chemical composition analyses for natural hokutolite crystals from various localities (Chen and Yu, 1984; Watanuki, 1990; Momoshima et al., 1997), the PbSO<sub>4</sub> content for this natural lead-bearing barite was approximately up to 47 mol%, which did not agree with the existence of the structure gap reported as above. Chen and Yu (1984) carried out a detailed substructural analysis on natural hokutolite grains and suggested that the hokutolite crystal contains a large number of coherent single crystal domains. Each domain is approximately 1 µm in dimension. This result showed that the natural hokutolites may be crystallized in an unstable geological environment and consequently have a poor crystallinity.

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In fact, a steady-state condition of growth for naturally precipitating hokutolite is unlikely to occur for a long period of time due to the change in chemical composition of hot spring water that is connected with volcanic activity supplying heat to the hot spring and the change in geographic situation by human activity (Momoshima et al., 1997).

Mineralogical study on hokutolite has by far been confined to its occurrence, genetics, chemistry and radioactivity. Detailed structural determinations of  $\text{BaSO}_4$ – $\text{PbSO}_4$  series have never been completed due to the poor quality of hokutolite crystals. Recently, maximum dimensions for the thick tabular single crystals over 0.1 mm and complete solid solutions between  $\text{BaSO}_4$  and  $\text{PbSO}_4$  were grown by a slow

precipitation procedure at about 95 °C (Lee and Yu, 1996). However, these synthetic crystals were not of good quality for crystal structure determination. In this paper, the principal object involves the synthesis of superior quality of single crystals of  $\text{BaSO}_4$ – $\text{PbSO}_4$  series and the crystal structure determination using single crystal X-ray diffraction analysis providing significant information in understanding the crystal structure of this solid solution series. We have also used Raman spectroscopy for analysis of the samples along barite-anglesite join because the Raman spectra of crystalline materials usually give rise to well-defined narrow bands and, therefore, both the frequencies and band widths can examine the effect of composition to the degree of possible cation ordering.

**Table 1.** Crystal data of various flux-grown  $(\text{Ba,Pb})\text{SO}_4$ .

|                                           | 1                                             | 2                                             | 3                                             | 4                                             | 5                                             | 6                                             | 7                                             |
|-------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| Chemical formula                          | $\text{PbSO}_4$                               | $(\text{Ba}_{.11}\text{Pb}_{.89})\text{SO}_4$ | $(\text{Ba}_{.14}\text{Pb}_{.86})\text{SO}_4$ | $(\text{Ba}_{.15}\text{Pb}_{.85})\text{SO}_4$ | $(\text{Ba}_{.29}\text{Pb}_{.71})\text{SO}_4$ | $(\text{Ba}_{.31}\text{Pb}_{.69})\text{SO}_4$ | $(\text{Ba}_{.32}\text{Pb}_{.68})\text{SO}_4$ |
| Space group                               | <i>Pnma</i>                                   | <i>Pnma</i>                                   | <i>Pnma</i>                                   | <i>Pnma</i>                                   | <i>Pnma</i>                                   | <i>Pnma</i>                                   | <i>Pnma</i>                                   |
| Unit cell                                 | $a = 8.475(2)$                                | $a = 8.511(1)$                                | $a = 8.511(1)$                                | $a = 8.532(1)$                                | $a = 8.578(1)$                                | $a = 8.594(1)$                                | $a = 8.575(2)$                                |
| Parameters (Å)                            | $b = 5.396(1)$                                | $b = 5.404(1)$                                | $b = 5.401(1)$                                | $b = 5.410(1)$                                | $b = 5.422(1)$                                | $b = 5.424(1)$                                | $b = 5.418(1)$                                |
|                                           | $c = 6.950(1)$                                | $c = 6.968(1)$                                | $c = 6.971(1)$                                | $c = 6.982(1)$                                | $c = 7.007(1)$                                | $c = 7.015(1)$                                | $c = 7.002(1)$                                |
| Cell volume (Å <sup>3</sup> )             | 317.8(1)                                      | 320.5(1)                                      | 320.4(1)                                      | 322.3(1)                                      | 325.9(1)                                      | 327.0(1)                                      | 325.3(1)                                      |
| Z                                         | 4                                             | 4                                             | 4                                             | 4                                             | 4                                             | 4                                             | 4                                             |
| Crystal size (μm)                         | 100 × 80 × 60                                 | 150 × 80 × 50                                 | 550 × 380 × 380                               | 370 × 320 × 240                               | 300 × 250 × 200                               | 200 × 200 × 100                               | 100 × 80 × 50                                 |
| $D_x$ (g/cm <sup>3</sup> )                | 6.338                                         | 6.142                                         | 6.077                                         | 6.042                                         | 5.766                                         | 5.719                                         | 5.730                                         |
| $\nu$ (mm <sup>−1</sup> )                 | 53.571                                        | 48.653                                        | 47.302                                        | 47.024                                        | 40.695                                        | 39.830                                        | 39.487                                        |
| Measured reflections                      | 1891                                          | 1897                                          | 1888                                          | 1759                                          | 1938                                          | 1805                                          | 1796                                          |
| Independent reflections ( $I > 3\sigma$ ) | 396                                           | 431                                           | 434                                           | 400                                           | 440                                           | 417                                           | 415                                           |
| Mean ( $I/\sigma$ )                       | 30.1                                          | 38.63                                         | 37.70                                         | 42.03                                         | 37.56                                         | 29.62                                         | 32.6                                          |
| Maximum $2\theta$ (°)                     | 55.00                                         | 56.50                                         | 56.68                                         | 55.72                                         | 56.60                                         | 55.99                                         | 56.41                                         |
| $R$ (%) ( $I > 2\sigma(I)$ )              | 3.83                                          | 6.77                                          | 5.33                                          | 5.10                                          | 3.94                                          | 1.83                                          | 2.70                                          |
| $R$ (%) (all data)                        | 4.27                                          | 7.10                                          | 5.65                                          | 5.32                                          | 4.13                                          | 2.06                                          | 2.95                                          |
| Largest $\Delta e/\text{Å}^3$             | +2.43/−1.57                                   | +5.59/−5.82                                   | +4.32/−4.52                                   | +5.25/−5.86                                   | +3.68/−2.49                                   | +1.25/−0.79                                   | +1.32/−1.64                                   |
|                                           | 8                                             | 9                                             | 10                                            | 11                                            | 12                                            | 13                                            | 14                                            |
| Chemical formula                          | $(\text{Ba}_{.48}\text{Pb}_{.52})\text{SO}_4$ | $(\text{Ba}_{.49}\text{Pb}_{.51})\text{SO}_4$ | $(\text{Ba}_{.66}\text{Pb}_{.34})\text{SO}_4$ | $(\text{Ba}_{.67}\text{Pb}_{.33})\text{SO}_4$ | $(\text{Ba}_{.68}\text{Pb}_{.32})\text{SO}_4$ | $(\text{Ba}_{.85}\text{Pb}_{.15})\text{SO}_4$ | $\text{BaSO}_4$                               |
| Space group                               | <i>Pnma</i>                                   | <i>Pnma</i>                                   | <i>Pnma</i>                                   | <i>Pnma</i>                                   | <i>Pnma</i>                                   | <i>Pnma</i>                                   | <i>Pnma</i>                                   |
| Unit cell                                 | $a = 8.663(1)$                                | $a = 8.659(1)$                                | $a = 8.701(2)$                                | $a = 8.705(2)$                                | $a = 8.708(2)$                                | $a = 8.812(1)$                                | $a = 8.896(1)$                                |
| Parameters (Å)                            | $b = 5.432(1)$                                | $b = 5.434(1)$                                | $b = 5.435(1)$                                | $b = 5.425(1)$                                | $b = 5.423(1)$                                | $b = 5.450(1)$                                | $b = 5.462(1)$                                |
|                                           | $c = 7.049(1)$                                | $c = 7.047(1)$                                | $c = 7.069(1)$                                | $c = 7.067(1)$                                | $c = 7.055(1)$                                | $c = 7.124(1)$                                | $c = 7.171(1)$                                |
| Cell volume (Å <sup>3</sup> )             | 331.7(1)                                      | 331.6(1)                                      | 334.3(1)                                      | 333.8(1)                                      | 333.2(1)                                      | 342.1(1)                                      | 348.4(1)                                      |
| Z                                         | 4                                             | 4                                             | 4                                             | 4                                             | 4                                             | 4                                             | 4                                             |
| Crystal size (μm)                         | 100 × 80 × 50                                 | 300 × 250 × 200                               | 150 × 100 × 80                                | 500 × 500 × 500                               | 300 × 250 × 200                               | 300 × 150 × 150                               | 330 × 250 × 150                               |
| $D_x$ (g/cm <sup>3</sup> )                | 5.347                                         | 5.395                                         | 5.096                                         | 5.107                                         | 5.106                                         | 4.733                                         | 4.449                                         |
| $\nu$ (mm <sup>−1</sup> )                 | 31.145                                        | 32.437                                        | 22.009                                        | 25.191                                        | 24.965                                        | 17.674                                        | 11.838                                        |
| Measured reflections                      | 1954                                          | 1802                                          | 1892                                          | 1963                                          | 2004                                          | 2001                                          | 2040                                          |
| Independent reflections ( $I > 3\sigma$ ) | 444                                           | 412                                           | 438                                           | 450                                           | 535                                           | 460                                           | 416                                           |
| Mean ( $I/\sigma$ )                       | 37.98                                         | 47.29                                         | 54.4                                          | 51.00                                         | 69.5                                          | 52.14                                         | 61.1                                          |
| Maximum $2\theta$ (°)                     | 56.59                                         | 55.70                                         | 56.56                                         | 56.54                                         | 59.77                                         | 56.46                                         | 56.53                                         |
| $R$ (%) ( $I > 2\sigma(I)$ )              | 5.63                                          | 4.03                                          | 5.58                                          | 5.61                                          | 4.16                                          | 2.71                                          | 2.49                                          |
| $R$ (%) (all data)                        | 5.71                                          | 4.17                                          | 5.67                                          | 5.79                                          | 4.19                                          | 2.76                                          | 2.54                                          |
| Largest $\Delta e/\text{Å}^3$             | +5.11/−5.13                                   | +3.03/−3.77                                   | +4.24/−3.80                                   | +5.19/−4.94                                   | +2.79/−2.10                                   | +1.15/−1.27                                   | +1.46/−1.25                                   |

**Table 2.** Atomic coordinates and their anisotropic thermal parameters of various flux-grown (Ba,Pb)SO<sub>4</sub>.

| Atoms                  |                        | 1          | 2          | 3          | 4          | 5          | 6          | 7          |
|------------------------|------------------------|------------|------------|------------|------------|------------|------------|------------|
| Pb/Ba                  | <i>x</i>               | 0.1879(1)  | 0.1870(1)  | 0.1867(1)  | 0.1868(1)  | 0.1861(1)  | 0.1857(1)  | 0.1862(1)  |
|                        | <i>y</i>               | 0.2500     | 0.2500     | 0.2500     | 0.2500     | 0.2500     | 0.2500     | 0.2500     |
|                        | <i>z</i>               | 0.1672(1)  | 0.1667(2)  | 0.1667(1)  | 0.1665(1)  | 0.1661(1)  | 0.1658(1)  | 0.1660(1)  |
|                        | sof                    | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        |
|                        | <i>U</i> <sub>11</sub> | 0.0023(1)  | 0.006(1)   | 0.005(1)   | 0.014(1)   | 0.006(1)   | 0.017(1)   | 0.016(1)   |
|                        | <i>U</i> <sub>22</sub> | 0.032(1)   | 0.014(1)   | 0.015(1)   | 0.026(1)   | 0.012(1)   | 0.018(1)   | 0.018(1)   |
|                        | <i>U</i> <sub>33</sub> | 0.037(1)   | 0.005(1)   | 0.010(1)   | 0.021(1)   | 0.015(1)   | 0.014(1)   | 0.017(1)   |
|                        | <i>U</i> <sub>13</sub> | 0.001(1)   | 0.001(1)   | 0.001(1)   | 0.001(1)   | 0.001(1)   | 0.001(1)   | 0.000(1)   |
|                        | S                      | <i>x</i>   | 0.4359(3)  | 0.4352(7)  | 0.4363(6)  | 0.4353(4)  | 0.4357(4)  | 0.4355(2)  |
| <i>y</i>               |                        | 0.7500     | 0.7500     | 0.7500     | 0.7500     | 0.7500     | 0.7500     | 0.7500     |
| <i>z</i>               |                        | 0.1844(4)  | 0.1864(8)  | 0.1859(7)  | 0.1858(6)  | 0.1866(5)  | 0.1862(2)  | 0.1860(4)  |
| sof                    |                        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        |
| <i>U</i> <sub>11</sub> |                        | 0.016(2)   | 0.004(3)   | 0.003(3)   | 0.010(2)   | 0.004(2)   | 0.014(1)   | 0.013(1)   |
| <i>U</i> <sub>22</sub> |                        | 0.019(2)   | 0.004(3)   | 0.007(3)   | 0.015(2)   | 0.003(2)   | 0.013(1)   | 0.011(1)   |
| <i>U</i> <sub>33</sub> |                        | 0.029(2)   | 0.000(3)   | 0.000(2)   | 0.013(2)   | 0.007(2)   | 0.012(1)   | 0.010(1)   |
| <i>U</i> <sub>13</sub> |                        | −0.001(1)  | 0.000(2)   | 0.000(2)   | 0.002(1)   | −0.001(1)  | 0.001(1)   | 0.001(1)   |
| O1                     |                        | <i>x</i>   | 0.3072(10) | 0.3093(22) | 0.3100(18) | 0.3097(11) | 0.3090(14) | 0.3087(5)  |
|                        | <i>y</i>               | 0.7500     | 0.7500     | 0.7500     | 0.7500     | 0.7500     | 0.7500     | 0.7500     |
|                        | <i>z</i>               | 0.0407(14) | 0.0467(32) | 0.0477(25) | 0.0487(21) | 0.0476(17) | 0.0472(7)  | 0.0464(13) |
|                        | sof                    | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        |
|                        | <i>U</i> <sub>11</sub> | 0.024(3)   | 0.017(11)  | 0.011(8)   | 0.020(5)   | 0.017(6)   | 0.027(3)   | 0.024(5)   |
|                        | <i>U</i> <sub>22</sub> | 0.030(4)   | 0.027(11)  | 0.032(11)  | 0.025(6)   | 0.017(7)   | 0.027(2)   | 0.025(5)   |
|                        | <i>U</i> <sub>33</sub> | 0.031(5)   | 0.001(9)   | 0.002(7)   | 0.014(6)   | 0.007(6)   | 0.015(2)   | 0.017(4)   |
|                        | <i>U</i> <sub>13</sub> | 0.005(3)   | −0.004(7)  | −0.001(6)  | −0.001(4)  | −0.006(4)  | −0.010(2)  | −0.006(3)  |
|                        | O2                     | <i>x</i>   | 0.4187(7)  | 0.4124(16) | 0.4170(13) | 0.4182(9)  | 0.4184(9)  | 0.4187(4)  |
| <i>y</i>               |                        | 0.9743(12) | 0.9718(24) | 0.9732(21) | 0.9735(17) | 0.9723(17) | 0.9716(6)  | 0.9718(11) |
| <i>z</i>               |                        | 0.3094(14) | 0.3086(17) | 0.3095(14) | 0.3080(12) | 0.3099(11) | 0.3093(4)  | 0.3098(8)  |
| sof                    |                        | 1.0        | 1.0        | 1.0        | 1.0        | 1.0        | 1.0        | 1.0        |
| <i>U</i> <sub>11</sub> |                        | 0.028(2)   | 0.015(7)   | 0.008(5)   | 0.019(3)   | 0.008(4)   | 0.026(2)   | 0.023(3)   |
| <i>U</i> <sub>22</sub> |                        | 0.021(3)   | 0.008(5)   | 0.000(6)   | 0.020(4)   | 0.010(4)   | 0.017(2)   | 0.011(3)   |
| <i>U</i> <sub>33</sub> |                        | 0.036(3)   | 0.001(5)   | 0.009(5)   | 0.025(5)   | 0.014(4)   | 0.019(1)   | 0.019(3)   |
| <i>U</i> <sub>23</sub> |                        | 0.001(3)   | −0.007(4)  | −0.001(4)  | −0.002(4)  | −0.007(3)  | −0.006(1)  | −0.005(2)  |
| <i>U</i> <sub>13</sub> |                        | −0.000(2)  | −0.014(4)  | −0.001(4)  | −0.004(3)  | 0.000(3)   | −0.003(1)  | −0.001(3)  |
| O3                     | <i>U</i> <sub>12</sub> | 0.000(2)   | 0.012(6)   | 0.010(1)   | 0.002(3)   | 0.001(3)   | 0.001(1)   | 0.003(2)   |
|                        | <i>x</i>               | 0.5929(11) | 0.5928(23) | 0.5945(19) | 0.5914(12) | 0.5922(13) | 0.5887(6)  | 0.5917(10) |
|                        | <i>y</i>               | 0.7500     | 0.7500     | 0.7500     | 0.7500     | 0.7500     | 0.7500     | 0.7500     |
|                        | <i>z</i>               | 0.0956(14) | 0.0944(27) | 0.0949(23) | 0.0990(19) | 0.0979(18) | 0.0958(7)  | 0.0957(13) |
|                        | sof                    | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        |
|                        | <i>U</i> <sub>11</sub> | 0.025(3)   | 0.010(9)   | 0.004(6)   | 0.010(5)   | 0.004(5)   | 0.019(3)   | 0.013(4)   |
|                        | <i>U</i> <sub>22</sub> | 0.043(6)   | 0.034(11)  | 0.035(11)  | 0.044(7)   | 0.025(7)   | 0.036(3)   | 0.036(5)   |
|                        | <i>U</i> <sub>33</sub> | 0.041(5)   | 0.000(8)   | 0.004(7)   | 0.021(7)   | 0.015(6)   | 0.031(3)   | 0.024(4)   |
|                        | <i>U</i> <sub>13</sub> | 0.010(3)   | 0.013(7)   | 0.012(6)   | 0.012(4)   | 0.008(4)   | 0.009(2)   | 0.012(3)   |
| Atoms                  |                        | 8          | 9          | 10         | 11         | 12         | 13         | 14         |
| Pb/Ba                  | <i>x</i>               | 0.1847(1)  | 0.1848(1)  | 0.1844(1)  | 0.1842(1)  | 0.1843(1)  | 0.1842(1)  | 0.1845(1)  |
|                        | <i>y</i>               | 0.2500     | 0.2500     | 0.2500     | 0.2500     | 0.2500     | 0.2500     | 0.2500     |
|                        | <i>z</i>               | 0.1643(1)  | 0.1645(1)  | 0.1637(1)  | 0.1631(1)  | 0.1627(1)  | 0.1607(1)  | 0.1584(1)  |
|                        | sof                    | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        |
|                        | <i>U</i> <sub>11</sub> | 0.017(1)   | 0.013(1)   | 0.001(1)   | 0.003(1)   | 0.022(1)   | 0.018(1)   | 0.009(1)   |
|                        | <i>U</i> <sub>22</sub> | 0.023(1)   | 0.020(1)   | 0.015(1)   | 0.001(1)   | 0.024(1)   | 0.014(1)   | 0.017(1)   |
|                        | <i>U</i> <sub>33</sub> | 0.007(1)   | 0.006(1)   | 0.017(1)   | 0.015(1)   | 0.024(1)   | 0.016(1)   | 0.014(1)   |
|                        | <i>U</i> <sub>13</sub> | 0.000(1)   | 0.000(1)   | 0.000(1)   | 0.000(1)   | 0.000(1)   | 0.000(1)   | 0.000(1)   |

**Table 2.** (Continued)

| Atoms |          | 8          | 9          | 10         | 11         | 12         | 13         | 14        |
|-------|----------|------------|------------|------------|------------|------------|------------|-----------|
| S     | x        | 0.4359(4)  | 0.4358(3)  | 0.4360(5)  | 0.4361(4)  | 0.4366(4)  | 0.4369(2)  | 0.4376(2) |
|       | y        | 0.7500     | 0.7500     | 0.7500     | 0.7500     | 0.7500     | 0.7500     | 0.7500    |
|       | z        | 0.1881(6)  | 0.1868(4)  | 0.1881(6)  | 0.1897(6)  | 0.1897(6)  | 0.1904(3)  | 0.1911(2) |
|       | sof      | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5       |
|       | $U_{11}$ | 0.015(2)   | 0.010(2)   | 0.002(2)   | 0.001(2)   | 0.019(2)   | 0.007(1)   | 0.010(1)  |
|       | $U_{22}$ | 0.014(2)   | 0.012(2)   | 0.008(2)   | 0.000(2)   | 0.015(2)   | 0.007(1)   | 0.014(1)  |
|       | $U_{33}$ | 0.003(2)   | 0.000(2)   | 0.015(2)   | 0.008(2)   | 0.017(2)   | 0.013(1)   | 0.012(1)  |
|       | $U_{13}$ | −0.000(1)  | 0.001(1)   | 0.001(1)   | 0.001(1)   | 0.001(1)   | 0.001(1)   | 0.001(1)  |
| O1    | x        | 0.3102(13) | 0.3111(9)  | 0.3144(14) | 0.3140(15) | 0.3137(14) | 0.3152(6)  | 0.3177(5) |
|       | y        | 0.7500     | 0.7500     | 0.7500     | 0.7500     | 0.7500     | 0.7500     | 0.7500    |
|       | z        | 0.0517(22) | 0.0494(18) | 0.0497(23) | 0.0463(23) | 0.0494(24) | 0.0496(10) | 0.0499(7) |
|       | sof      | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5       |
|       | $U_{11}$ | 0.035(8)   | 0.025(5)   | 0.017(8)   | 0.029(9)   | 0.036(8)   | 0.018(3)   | 0.021(2)  |
|       | $U_{22}$ | 0.032(7)   | 0.031(6)   | 0.025(7)   | 0.006(6)   | 0.036(8)   | 0.019(3)   | 0.026(3)  |
|       | $U_{33}$ | 0.000(7)   | 0.000(5)   | 0.023(7)   | 0.007(7)   | 0.022(7)   | 0.020(3)   | 0.016(2)  |
|       | $U_{13}$ | −0.008(4)  | −0.007(3)  | −0.007(5)  | −0.012(5)  | −0.013(5)  | −0.010(2)  | −0.008(2) |
| O2    | x        | 0.4193(10) | 0.4197(7)  | 0.4206(9)  | 0.4189(10) | 0.4190(11) | 0.4192(4)  | 0.4193(3) |
|       | y        | 0.9723(16) | 0.9713(12) | 0.9710(18) | 0.9699(17) | 0.9729(19) | 0.9713(7)  | 0.9709(6) |
|       | z        | 0.3103(11) | 0.3102(9)  | 0.3111(11) | 0.3104(12) | 0.3111(12) | 0.3109(5)  | 0.3113(4) |
|       | sof      | 1.0        | 1.0        | 1.0        | 1.0        | 1.0        | 1.0        | 1.0       |
|       | $U_{11}$ | 0.028(4)   | 0.020(3)   | 0.003(4)   | 0.013(4)   | 0.030(4)   | 0.015(2)   | 0.015(2)  |
|       | $U_{22}$ | 0.020(4)   | 0.013(3)   | 0.020(4)   | 0.000(4)   | 0.019(4)   | 0.008(2)   | 0.017(2)  |
|       | $U_{33}$ | 0.004(4)   | 0.007(3)   | 0.018(4)   | 0.011(4)   | 0.022(3)   | 0.019(2)   | 0.019(1)  |
|       | $U_{23}$ | −0.004(3)  | −0.004(2)  | −0.004(3)  | −0.007(3)  | −0.005(3)  | −0.003(2)  | −0.004(1) |
| O3    | $U_{13}$ | −0.004(3)  | −0.001(2)  | −0.000(3)  | −0.000(3)  | 0.001(3)   | −0.000(1)  | −0.001(1) |
|       | $U_{12}$ | 0.003(3)   | 0.010(2)   | 0.000(3)   | 0.005(3)   | −0.002(3)  | 0.000(2)   | 0.001(1)  |
|       | x        | 0.5877(14) | 0.5896(11) | 0.5895(14) | 0.5874(14) | 0.5902(14) | 0.5876(7)  | 0.5882(5) |
|       | y        | 0.7500     | 0.7500     | 0.7500     | 0.7500     | 0.7500     | 0.7500     | 0.7500    |
|       | z        | 0.0980(19) | 0.0991(15) | 0.0995(21) | 0.0988(22) | 0.1010(21) | 0.1036(9)  | 0.1074(7) |
|       | sof      | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5        | 0.5       |
|       | $U_{11}$ | 0.022(5)   | 0.015(4)   | 0.001(5)   | 0.001(5)   | 0.021(5)   | 0.012(3)   | 0.012(2)  |
|       | $U_{22}$ | 0.039(7)   | 0.034(5)   | 0.034(7)   | 0.016(6)   | 0.033(7)   | 0.028(3)   | 0.036(3)  |
|       | $U_{33}$ | 0.015(7)   | 0.021(6)   | 0.031(7)   | 0.029(8)   | 0.037(7)   | 0.031(3)   | 0.029(2)  |
|       | $U_{13}$ | −0.045(5)  | 0.009(4)   | 0.006(5)   | 0.017(6)   | 0.013(5)   | 0.009(3)   | 0.010(2)  |

## Experimental procedures

### Crystal synthesis

Crystal syntheses of (Ba,Pb)SO<sub>4</sub> solid solutions were carried out by the flux evaporation method. Powders of BaSO<sub>4</sub> and PbSO<sub>4</sub> in appropriate proportion were used as the starting materials and Na<sub>2</sub>SO<sub>4</sub> was added as the flux substance. The mixture of the known composition placed in a platinum crucible was heated up to temperature of 750–850 °C and held at the temperature for a period of 20–30 hours. In order to avoid sudden cooling of the crystal grown, the temperature of the furnace was lowered to 700 °C at a cooling rate of 2 °C/hr. The details of the (Ba,Pb)SO<sub>4</sub> synthesis by the flux evaporation method were reported by Wang et al. (2002).

### Crystal characterizations

The chemical compositions of the synthetic samples of BaSO<sub>4</sub>–PbSO<sub>4</sub> series were determined using a computer-

controlled JEOL JXA-8900R electron probe X-ray micro-analyzer, which was operated with the conditions of a 15 kV accelerating voltage, a 10 nA probe current, a 10 µm beam diameter and a counting time of 20 seconds for each element. Data reductions for the atomic number effect, absorption and fluorescence were made with the program of the ZAF correction. The synthetic crystals were selected for indexing and intensity data collection at 293 K. The measurements were performed on a Bruker Smart-CCD diffractometer system equipped with a normal focus, 3 kW sealed-tube X-ray MoK<sub>α</sub> source ( $\lambda = 0.71073$  Å). Intensity data were collected in 1271 frames with increasing  $\omega$  (0.3° per frame) and corrected for  $Lp$  and absorption effects. Unit cell dimensions were determined by a least-squares fit of collected reflections. Structures of crystals were analyzed and refined with a full-matrix least-squares method of the SHELXTAL PLUS program. The structure analysis and refinement procedures were based on the reflections with  $I > 2\sigma(I)$ . The intensities of the equivalent reflections were also averaged. A series of synthetic crystals with different BaSO<sub>4</sub> content

were also measured and refined as above. Unit-cell and data collection parameters are summarized in Table 1. The atomic coordinates and the anisotropic temperature factors of the synthetic (Ba,Pb)SO<sub>4</sub> refined in this study are listed in Table 2. Both the interatomic distances and bond angles are listed in Table 3. Raman spectroscopy measurements were carried out with the use of a Dilor X-Y unit. A coherent argon ion laser source with a beam of 514.5 nm wavelength was employed in this work, and the operation power of the laser was kept at 50mW with the counting time of 60 seconds.

## Results and discussion

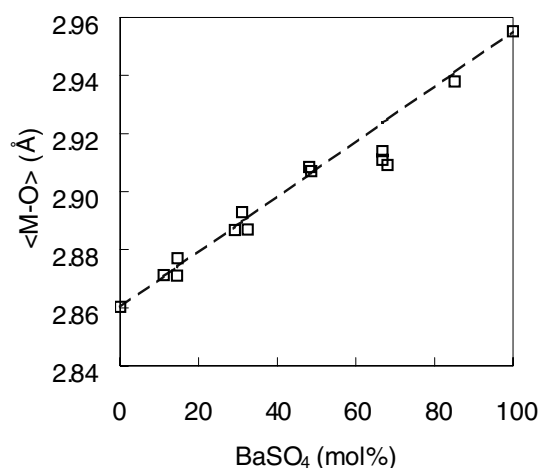
### Crystal structures

A series of the synthetic (Ba,Pb)SO<sub>4</sub> crystals have an orthorhombic form with the space group *Pnma* and their basic crystal data are summarized in Table 1 and 3. We find that they are similar to barite structure through the single crystal X-ray diffraction investigations. This structure is composed of isolated SO<sub>4</sub> groups that are approximately regular tetrahedra with similar sulfur-oxygen (S–O)

**Table 3.** Bond distances and selected bond angles of various flux-grown (Ba,Pb)SO<sub>4</sub>.

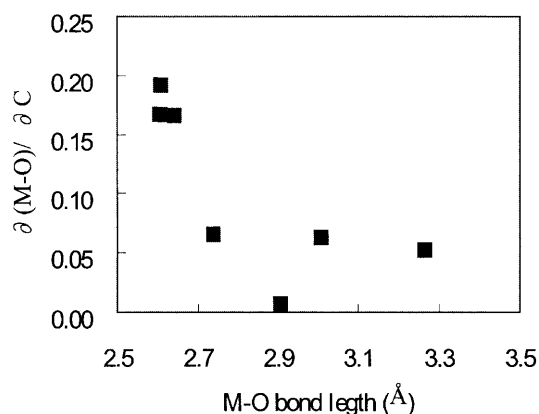
|                           | 1         | 2         | 3         | 4         | 5         | 6        | 7        |
|---------------------------|-----------|-----------|-----------|-----------|-----------|----------|----------|
| Distances (Å)             |           |           |           |           |           |          |          |
| S–O1                      | 1.471(8)  | 1.447(2)  | 1.443(2)  | 1.448(12) | 1.460(12) | 1.462(5) | 1.457(8) |
| S–O2 (2×)                 | 1.495(6)  | 1.483(12) | 1.491(11) | 1.487(9)  | 1.490(8)  | 1.487(3) | 1.488(6) |
| S–O3                      | 1.468(9)  | 1.488(2)  | 1.488(2)  | 1.463(10) | 1.480(11) | 1.462(5) | 1.482(8) |
| Mean                      | 1.482     | 1.475     | 1.478     | 1.471     | 1.479     | 1.474    | 1.479    |
| Angles (°)                |           |           |           |           |           |          |          |
| O1–S–O2                   | 108.2(3)  | 106.8(7)  | 107.7(6)  | 107.8(4)  | 108.2(5)  | 108.4(2) | 108.7(3) |
| O1–S–O3                   | 113.0(6)  | 112.1(12) | 112.9(9)  | 114.2(8)  | 113.3(7)  | 112.5(3) | 112.6(5) |
| O2–S–O2                   | 107.8(5)  | 107.8(11) | 107.9(9)  | 108.8(8)  | 107.9(7)  | 107.9(2) | 107.7(5) |
| O2–S–O3                   | 109.7(3)  | 111.5(8)  | 110.2(6)  | 109.1(4)  | 109.5(4)  | 109.8(2) | 109.5(3) |
| Distances (Å)             |           |           |           |           |           |          |          |
| <i>M</i> <sup>a</sup> –O3 | 2.606(9)  | 2.610(2)  | 2.607(2)  | 2.649(11) | 2.653(11) | 2.669(5) | 2.643(8) |
| <i>M</i> –O1              | 2.609(9)  | 2.648(2)  | 2.669(2)  | 2.669(8)  | 2.673(12) | 2.676(5) | 2.664(9) |
| <i>M</i> –O2 (2×)         | 2.642(6)  | 2.630(11) | 2.658(11) | 2.667(8)  | 2.693(8)  | 2.703(3) | 2.697(6) |
| <i>M</i> –O2 (2×)         | 2.738(6)  | 2.784(14) | 2.742(12) | 2.742(8)  | 2.751(8)  | 2.753(3) | 2.747(6) |
| <i>M</i> –O2 (2×)         | 2.907(7)  | 2.895(13) | 2.921(11) | 2.921(9)  | 2.913(8)  | 2.917(3) | 2.912(6) |
| <i>M</i> –O1 (2×)         | 3.007(3)  | 3.014(9)  | 3.010(7)  | 3.010(5)  | 3.025(6)  | 3.027(2) | 3.026(4) |
| <i>M</i> –O3 (2×)         | 3.265(6)  | 3.275(12) | 3.265(10) | 3.265(8)  | 3.276(7)  | 3.294(3) | 3.283(5) |
| Mean                      | 2.861     | 2.871     | 2.871     | 2.877     | 2.887     | 2.894    | 2.883    |
|                           | 8         | 9         | 10        | 11        | 12        | 13       | 14       |
| Distances (Å)             |           |           |           |           |           |          |          |
| S–O1                      | 1.453(13) | 1.450(10) | 1.438(14) | 1.468(14) | 1.458(13) | 1.468(6) | 1.470(5) |
| S–O2 (2×)                 | 1.490(8)  | 1.491(6)  | 1.487(9)  | 1.474(8)  | 1.489(9)  | 1.489(4) | 1.492(3) |
| S–O3                      | 1.460(12) | 1.468(9)  | 1.472(13) | 1.466(12) | 1.477(12) | 1.465(6) | 1.469(5) |
| Mean                      | 1.473     | 1.475     | 1.471     | 1.471     | 1.478     | 1.478    | 1.481    |
| Angles (°)                |           |           |           |           |           |          |          |
| O1–S–O2                   | 108.1(5)  | 108.6(4)  | 109.2(5)  | 109.0(5)  | 108.4(5)  | 108.5(2) | 108.6(2) |
| O1–S–O3                   | 112.8(8)  | 113.2(6)  | 112.0(9)  | 110.3(9)  | 112.2(9)  | 112.0(4) | 112.3(3) |
| O2–S–O2                   | 108.3(7)  | 107.6(5)  | 107.7(7)  | 108.1(8)  | 108.5(5)  | 108.2(3) | 108.0(3) |
| O2–S–O3                   | 109.8(5)  | 109.3(3)  | 109.3(5)  | 110.2(5)  | 109.7(5)  | 109.8(2) | 109.7(2) |
| Distances (Å)             |           |           |           |           |           |          |          |
| <i>M</i> –O3              | 2.703(12) | 2.696(10) | 2.701(13) | 2.716(12) | 2.705(13) | 2.755(6) | 2.777(5) |
| <i>M</i> –O1              | 2.731(2)  | 2.713(13) | 2.724(2)  | 2.708(2)  | 2.728(20) | 2.771(7) | 2.808(5) |
| <i>M</i> –O2 (2×)         | 2.732(9)  | 2.736(6)  | 2.752(9)  | 2.751(9)  | 2.744(10) | 2.782(4) | 2.809(3) |
| <i>M</i> –O2 (2×)         | 2.756(9)  | 2.756(6)  | 2.751(9)  | 2.771(9)  | 2.762(9)  | 2.793(4) | 2.817(3) |
| <i>M</i> –O2 (2×)         | 2.915(9)  | 2.915(7)  | 2.910(9)  | 2.905(9)  | 2.902(9)  | 2.915(4) | 2.916(3) |
| <i>M</i> –O1 (2×)         | 3.031(6)  | 3.039(5)  | 3.048(6)  | 3.052(7)  | 3.043(7)  | 3.063(3) | 3.077(2) |
| <i>M</i> –O3 (2×)         | 3.300(8)  | 3.292(6)  | 3.293(8)  | 3.303(9)  | 3.287(9)  | 3.312(4) | 3.320(3) |
| Mean                      | 2.908     | 2.907     | 2.911     | 2.915     | 2.909     | 2.938    | 2.955    |

a: *M* = Ba/Pb

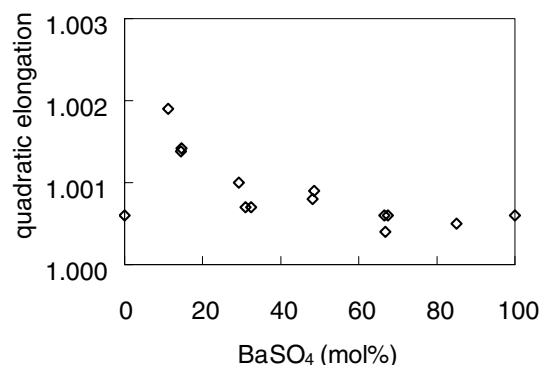
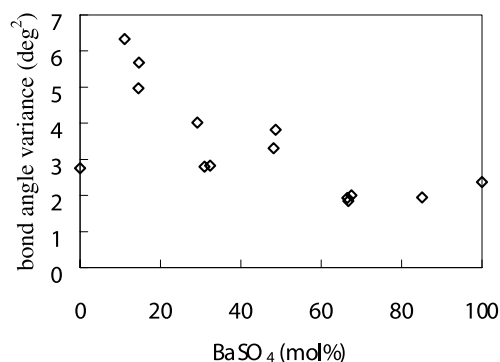


**Fig. 1.** The average  $M$ -O bond length (Å) plotted against the mole fraction of barium sulfate.

bond lengths. The divalent atoms of Pb, Ba or Sr (which we refer to as metal or  $M$ ) are 12-coordinated to join the  $\text{SO}_4$  tetrahedra to form the isostructural sulfates. The metal-oxygen ( $M$ -O) bond lengths in each crystal are dissimilar and vary as much as 25.5%. The present study reveals that the average  $M$ -O bond lengths increase with increasing Ba of the metal atom owing to the smaller ionic radius of Pb (1.50 Å) than that of Ba (1.61 Å) (Fig. 1). In Fig. 2, we examined the variation of each  $M$ -O bond versus the composition of the flux-grown  $(\text{Ba,Pb})\text{SO}_4$  crystals. The seven non-equivalent  $M$ -O bonds in the 12-coordinated polyhedra were regressed against composition, and the slope,  $\partial(M\text{-O})/\partial C$ , was plotted against the  $M$ -O bond lengths of  $\text{PbSO}_4$  in Fig. 2, where  $C$  represents the  $\text{BaSO}_4$  content. This plot illustrates that as the average size of the  $M$  cation increases, the short  $M$ -O bonds generally tend to increase at a substantially greater rate than the longer  $M$ -O bonds, resulting in a more regular coordination. The similar trend was also reported by Jacobsen et al. (1998). Nevertheless, the variation of the  $M$ -O length of about 2.9 Å seems to be insignificant with increasing  $\text{BaSO}_4$  content. Moreover, as the Ba content increases, the S- $M$  distance and O- $M$  distance increase, hence reducing the Coulomb interactions that cause the skewing of the tetrahedron. Regular polyhedra have a quadratic elongation ( $\lambda$ ) of one and a bond angle variance ( $\sigma$ ) of zero. These val-



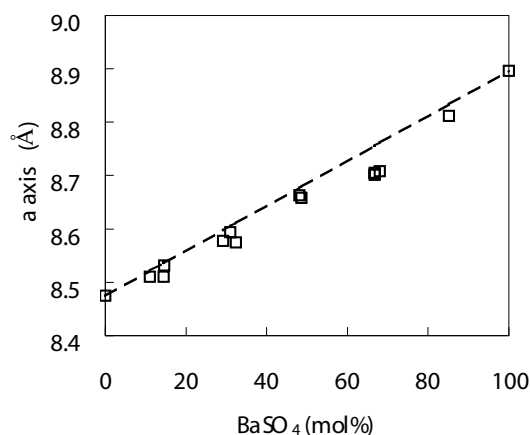
**Fig. 2.** A plot of the slope  $\partial(M\text{-O})/\partial C$  versus the  $M$ -O bond length, obtained in the regression of  $M$ -O bond length.



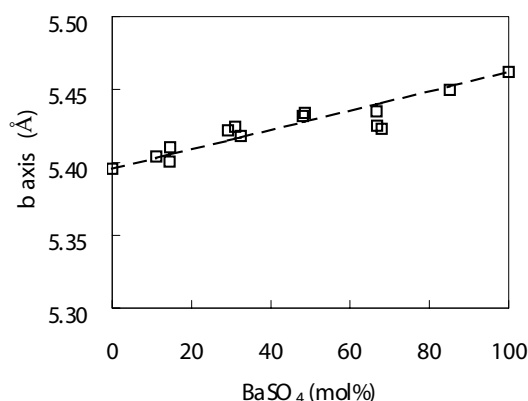
**Fig. 3.** Variation of bond angle variance ( $\sigma$ ) and quadratic elongation ( $\lambda$ ) with changing  $\text{BaSO}_4$  content.

ues increase with distortion of polyhedra and can be calculated after Robinson et al. (1971). The calculated bond angle variance and quadratic elongation of the  $\text{SO}_4$  tetrahedron with changing  $\text{BaSO}_4$  contents are shown in Fig. 3. As shown in Fig. 3, the tetrahedron is distorted to a certain extent near the  $\text{PbSO}_4$  end and becomes more regular as the Ba/Pb ratio increases. Therefore, the trend is that as the mean  $M$  cation size increases, the S-O tetrahedron also becomes more regular. Furthermore, It is also noteworthy from Fig. 3 that the initial distortion is intensified as bigger Ba ion replaces smaller Pb ion in the  $M$  site and then gradually reduced due to the decrease in the Coulomb interactions.

The measurements on the unit cell parameters and the cell volumes with different chemical compositions are shown in Figs. 4, 5, 6, and 7. It is clear from these plots

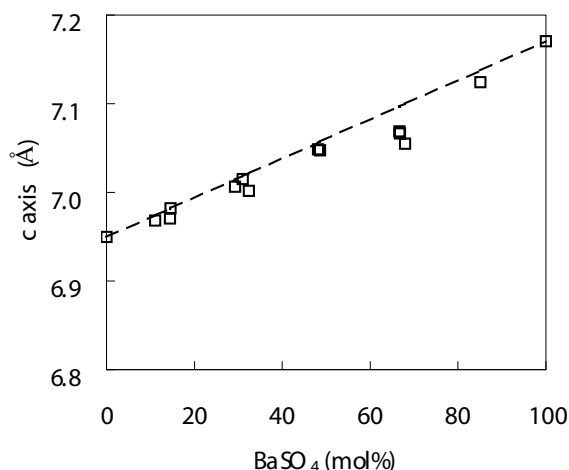


**Fig. 4.** The length of the  $a$ -axis versus the mole fraction of barium sulfate.

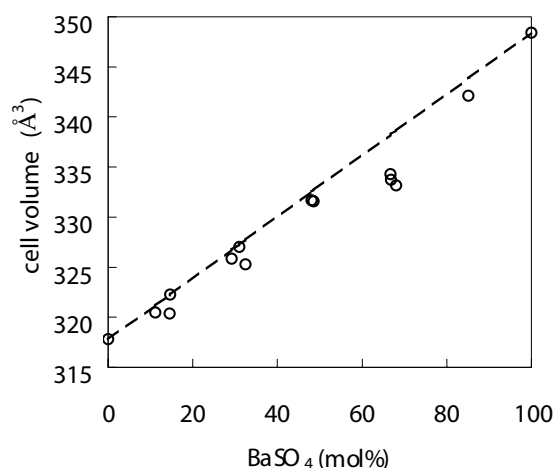


**Fig. 5.** The length of the  $b$ -axis versus the mole fraction of barium sulfate.

that the unit cell constants increase with increasing BaSO<sub>4</sub> contents in the synthetic crystals. However, the variations in dimension of the  $a$ - and  $c$ -axes with the BaSO<sub>4</sub> content are more significant than that of the  $b$ -axis. The deviations from linearity of all the unit cell axes can also be observed in Figs. 4, 5 and 6. The changes in the unit-cell parameters associated with Ba–Pb substitution have been calculated. If one takes a look at the difference in cell parameters between the barite and anglesite, in terms of the relative change  $\Delta a = (a_{\text{barite}} - a_{\text{anglesite}})/a_{\text{anglesite}}$  of a cell parameter  $a$ , the relative expansion along the  $b$ -axis is the lowest with adding Ba ( $\Delta a = 5.0\%$ ,  $\Delta b = 1.2\%$ ,  $\Delta c = 3.2\%$ ). This is important when trying to understand the change in crystal structures of this solid solution series. To our knowledge, the barite structure is constrained by symmetry conditions, with the Ba, Pb, S, and half the O atoms lying on mirror planes perpendicular to the  $b$ -axis (Deer et al., 1992). The interplay of these symmetry factors with the size difference between the Ba and Pb ions may account for the observed shapes of the graphs of unit cell parameters versus composition. Thus away from the pure compound end members, the structure roughly packs more efficiently than the expected ones in the  $a$ - and  $c$ -axes directions (i.e. within and parallel to the mirror planes), while the distance between mirror planes is less accommodating and increases the  $b$ -axis length above the

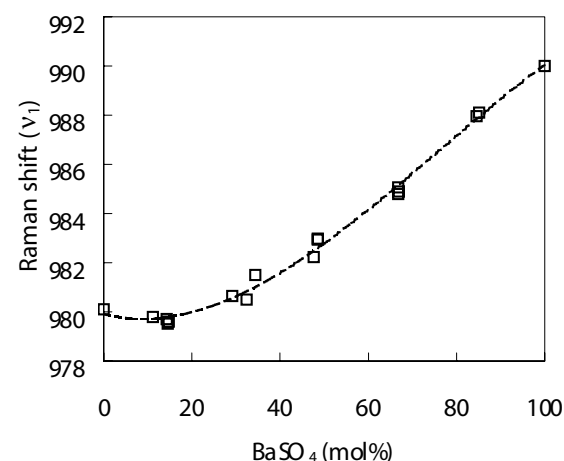


**Fig. 6.** The length of the  $c$ -axis versus the mole fraction of barium sulfate.



**Fig. 7.** The unit cell volume versus the mole fraction of barium sulfate.

expected mean. The similar results are also presented in BaSO<sub>4</sub>–SrSO<sub>4</sub> solid solution (Goldish, 1989). The variation in the unit cell volume, as shown in Fig. 7, is also consistent with its dependence on the contents of BaSO<sub>4</sub> in the synthetic samples. The cell volumes of this series are a little smaller than those calculated from molar ratio of lead to barium on the basis of the Vegard's law. In fact, deviations from Vegard's law for these crystals are perhaps not surprising, since the law was for metals and alloys, where a simple sphere contact model may be expected to hold, whereas in the more complex barite structure this principle is no longer valid. However, these measurements are in reasonable agreement with the result by Sasaki and Minato (1982), who examined the lattice constants of 26 natural lead-bearing barite specimens (hokutolite). They found that small amounts of strontium ions were probably responsible for the negative deviations of unit cell volume from Vegard's rule owing that these smaller ions may occupy the regular cation sites in the barite structure. Although small amounts of strontium concentrations (<0.18wt% SrO) were also detected in our synthetic crystals, it seems not likely to give rise to the anomalously negative deviations since Sr concentrations are relatively low in the flux-grown crystals with a composition around 70% of BaSO<sub>4</sub>. Therefore, another mechanism plays an



**Fig. 8.** Raman shift of  $\nu_1$  band as a function of BaSO<sub>4</sub> content.

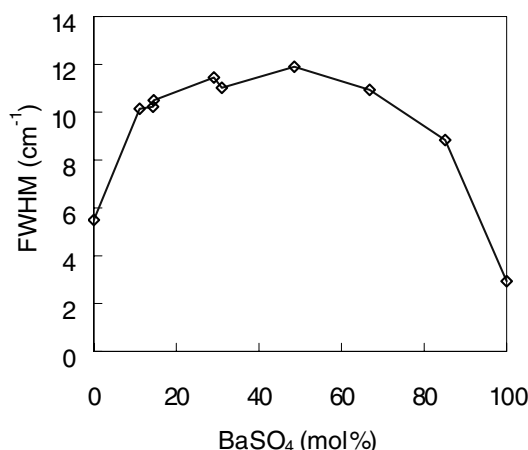


Fig. 9. The half width of  $\nu_1$  band as a function of BaSO<sub>4</sub> content.

important role in determining the structural behavior. The anomalous deviations previously mentioned are fairly consistent with the result reported by Takano et al. (1969). They indicated that a structure gap exists in the composition of about 75 mol% of BaSO<sub>4</sub> on the basis of some measurements. As shown in Fig. 1, the average *M*-O bond lengths as a function of the BaSO<sub>4</sub> content display a nearly linear increase. However, it is noticed that discontinuities in *M*-O bond are apparent at approximately 70% of BaSO<sub>4</sub>. The increase of the mean *M*-O bond lengths seem to be somewhat small with the increase in BaSO<sub>4</sub> content approaching to the above composition. Furthermore, the crystal structures determined by a four-circle single crystal diffractometer are all similar to the barite structure in these crystals. The Ba-Pb distribution is disordered after substitution, meaning that the Ba and Pb ions are randomly substituted in the *M* sites of a barite structure. Hence, the abnormally negative deviations of all unit cell parameters from Vegard's rule are primarily attributed to the discontinuities in mean *M*-O bond lengths.

In addition, Jacobsen et al. (1998) examined the barite structures as a function of the occupancy of the *M* site. They found that the SO<sub>4</sub> tetrahedra rotate around the axis perpendicular to the mirror plane and through the sulfur positions. However, the rotation is not obvious in the present samples as the Ba/Pb ratio increases.

### Raman spectral observations

The peak corresponding to the symmetric stretching mode ( $\nu_1$ ) of the S-O bond in the sulfates appears to be the strongest in the Raman scattering intensity. Figure 8 shows the Raman spectra region of this  $\nu_1$  mode in several samples of the BaSO<sub>4</sub>-PbSO<sub>4</sub> solid solution. The frequency of a Raman shift is determined by the bond strength and the atomic masses (Fadini and Schnepel, 1989). Therefore, the  $\nu_1$  frequency is a function of S-O stretching force constant in sulfates and, in general, increases with an increase in the force constant. The force constants of SO<sub>4</sub> tetrahedra were calculated from the bond lengths and the infrared absorption frequencies by Miyake et al. (1978). The stretching force constants for barite, and anglesite are  $K = 6.27$  and  $5.98$  mdyn/Å, respectively. Therefore, this systematic frequency shift is largely due to

the increase of mean force constants because of substitution of larger cations in the *M* sites. However,  $\nu_1$  frequency slightly decreases with a composition lower than 20% of BaSO<sub>4</sub> content.

The barite structure is similar to the nesosilicate structure in the sense that both are comprised of isolated tetrahedra (SO<sub>4</sub> versus SiO<sub>4</sub>) joined by divalent atoms. Lam et al. (1990) found that  $\nu_1$  of forsterite is also sensitive to O-O force constants. However, the value of O-O force constant is significantly smaller than that of Si-O. There is a significant change in the intertetrahedral O-O distances, about 6% from PbSO<sub>4</sub> to BaSO<sub>4</sub>. The dominant contribution to the O-O force constant comes from the Coulomb interaction. We estimated that a 6% increase in distance may cause a 12% decrease in the Coulomb force constants. Moreover, Mohanan et al. (1993) indicated that a systematic high-frequency decrease of Si-O bands is attributed to increasing the distortion of SiO<sub>4</sub> tetrahedra in the olivine structure. The tendency may also be valid for qualitative Raman spectral analyses of the solid solution series because of the similarity between SO<sub>4</sub> and SiO<sub>4</sub> tetrahedra as mentioned above. Accordingly, the increase of SO<sub>4</sub> distortions caused by the ionic substitution of bigger Ba for Pb for samples of low Ba/Pb molar ratio may also result in a small shift downward in the Raman frequency of PbSO<sub>4</sub> end. It is therefore inferred that the small decrease in  $\nu_1$  frequency with BaSO<sub>4</sub> contents being smaller than 20 mol% may be attributed to the net effect of the S-O force constants, intertetrahedral O-O force constants, and distortions of SO<sub>4</sub> tetrahedra.

In vibrational spectroscopy, the half width of a Raman band indicates positional disorder in crystal structures (Mohanan et al., 1993). The line width observed for some solid solution systems often exhibits a local maximum around 50 mol% substitution (Panitz, et al., 2000). In this study, the similar ionic radii of the same valent cations are employed and thus substitutional solid solution are also formed. Random substitution of Ba for Pb results in differences in the immediate cation neighborhood of sulfate ions. These differences mainly account for the broadening in line widths of Raman bands as a function of barium concentration (Fig. 9). On the other hand, Raman scattering from well-ordered BaSO<sub>4</sub> and PbSO<sub>4</sub> crystals produces narrow lines. As can be seen from Fig. 9, precise line widths, measured on the most intense line ( $\nu_1$ ), show a pronounced maximum in the middle of the solid solution series and demonstrate the relationship between Raman line width and cation disorder. This result shows that Raman line widths are sensitive to very small variations in ionic size, even when the ions have the same charge and the same coordination number.

### Summary

The flux-grown (Pb,Ba)SO<sub>4</sub> crystals with barite structure were synthesized with the use of the mixture of BaSO<sub>4</sub> and PbSO<sub>4</sub>, and a flux agent of Na<sub>2</sub>SO<sub>4</sub>. The present study supported the existence of a complete solid solution series for the PbSO<sub>4</sub>-BaSO<sub>4</sub> binary system. X-ray diffraction work on the synthetic samples shows that the unit cell

parameters increase with an increasing BaSO<sub>4</sub> content. We verify the nonlinear behavior of the unit cell dimensions with composition. This work elucidates that as the BaSO<sub>4</sub> content increases, the shorter *M*-O bonds tend to increase more than the longer *M*-O bonds. The observed trends also indicate that the *M* atoms exhibit more regular polyhedron, and the SO<sub>4</sub> tetrahedra become closer to the ideal form as the BaSO<sub>4</sub> content increases. The variations in the average *M*-O bond lengths result in the significant negative deviations of all unit cell parameters around 70 mol% of BaSO<sub>4</sub> for our synthetic crystals. This result may explain the occurrence of the structural gap in natural hokutolite samples.

The Raman spectra recorded for samples with various BaSO<sub>4</sub> contents display a continuous change in both peak positions and peak widths. The slight decrease in  $\nu_1$  frequency for crystals with low Ba/Pb ratio may be attributed to the net effect of the S–O force constants, intertetrahedral O–O force constants, and distortions of SO<sub>4</sub> tetrahedra. The present results also indicate that the disorder of mixed *M* cations along solid solution series is responsible for the Raman line broadening with the local maximum in the line width plot occurring at about 50 mol% substitution. These experimental results demonstrate that variations of Raman shift of  $\nu_1$  peak and its line width are essentially associated with the random Pb–Ba substitution in the synthetic crystals.

**Acknowledgments.** The authors are grateful to Miss F. L. Liao who collected the X-ray intensity data. We also thank Mr. H. D. Jiang of the Dr. Sun Yat-sen Memorial University for providing assistance in the EPMA operation. Thanks are also extended to Miss E. P. Huang for her kind assistance in Raman spectroscopy measurements. The authors also thank two anonymous reviewers for their careful and constructive reviews which greatly improve the manuscript. This work was supported by grants NSC90-2116–M153-001 from the National Science Council of Republic of China.

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