High-pressure Raman spectroscopic studies on orthophosphates 
Ba$_3$(PO$_4$)$_2$ and Sr$_3$(PO$_4$)$_2$

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**Abstract**

By using diamond anvil cell (DAC), high-pressure Raman spectroscopic studies of orthophosphates Ba$_3$(PO$_4$)$_2$ and Sr$_3$(PO$_4$)$_2$ were carried out up to 30.7 and 30.1 GPa, respectively. No pressure-induced phase transition was found in the studies. A methanol:ethanol:water (16:3:1) mixture was used as pressure medium in DAC, which is expected to exhibit nearly hydrostatic behavior up to about 14.4 GPa at room temperature. The behaviors of the phosphate modes in Ba$_3$(PO$_4$)$_2$ and Sr$_3$(PO$_4$)$_2$ below 14.4 GPa were quantitatively analyzed. The Raman shift of all modes increased linearly and continuously with pressure in Ba$_3$(PO$_4$)$_2$ and Sr$_3$(PO$_4$)$_2$. The pressure coefficients of the phosphate modes in Ba$_3$(PO$_4$)$_2$ range from 2.8179 to 3.4186 cm$^{-1}$ GPa$^{-1}$ for $\nu_1$, 2.9609 cm$^{-1}$ GPa$^{-1}$ for $\nu_2$, from 0.9855 to 1.8085 cm$^{-1}$ GPa$^{-1}$ for $\nu_4$, and 1.4330 cm$^{-1}$ GPa$^{-1}$ for $\nu_5$, and the pressure coefficients of the phosphate modes in Sr$_3$(PO$_4$)$_2$ range from 3.4247 to 4.3765 cm$^{-1}$ GPa$^{-1}$ for $\nu_3$, 3.7808 cm$^{-1}$ GPa$^{-1}$ for $\nu_4$, from 1.1005 to 1.9244 cm$^{-1}$ GPa$^{-1}$ for $\nu_5$, and 1.5647 cm$^{-1}$ GPa$^{-1}$ for $\nu_6$.

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1. Introduction

Alkaline earth metal orthophosphates, such as Ba$_3$(PO$_4$)$_2$ and Sr$_3$(PO$_4$)$_2$, are important substances for photoluminescence when they are doped with Eu$^{2+}$ or Yb$^{2+}$ [1–5]. In earth science, the orthophosphates of strontium and barium have been reported to be isomorphous with orthovanadates and orthoarsenates of the same alkaline earth elements [6–8]. On the other hand, $\gamma$-Ca$_3$(PO$_4$)$_2$, a typical analog of Ba$_3$(PO$_4$)$_2$ and Sr$_3$(PO$_4$)$_2$, has been named as tuite, and regarded as an important host for very large lithophile elements and rare earth elements in the upper mantle because it is one of the decomposed products of apatites [9–11]. The $\gamma$-Ca$_3$(PO$_4$)$_2$ is stable at least in the upper mantle [11], therefore, Ba$_3$(PO$_4$)$_2$ and Sr$_3$(PO$_4$)$_2$ may also be stable in the deep mantle as potential phosphorus hosts as well as rare earth elements.

The crystal analysis indicates that Ba$_3$(PO$_4$)$_2$ and Sr$_3$(PO$_4$)$_2$ are isostructural and rhombohedral in symmetry with the space group R-3m (No. 166, $Z = 3$) [6,12,13]. In the crystal structure (Fig. 1), a phosphorus atom is tetrahedrally coordinated by oxygen atoms and metal cations occupy two types of large metal sites. The Ba(1) or Sr(1) site has twelve oxygen neighbors and the Ba(2) or Sr(2) site is coordinated by ten oxygen atoms. The structure is characterized by the translationally interconnected polyhedral sequence PO$_4$·M(2)O$_{10}$·M(1)O$_{12}$·M(2)O$_{10}$·PO$_4$ (M = Ba or Sr) in the direction of the c axis [12].

**Fig. 1.** The crystal structure of Ba$_3$(PO$_4$)$_2$ and Sr$_3$(PO$_4$)$_2$.

The physical properties of Ba$_3$(PO$_4$)$_2$ and Sr$_3$(PO$_4$)$_2$ at ambient conditions have been reported in literatures [14–16]. In previous studies [17,18], the physical properties of $\gamma$-Ca$_3$(PO$_4$)$_2$ under high pressure have been examined by in situ X-ray diffraction and Raman spectroscopy. However, the physical behaviors of the orthophosphates Ba$_3$(PO$_4$)$_2$ and Sr$_3$(PO$_4$)$_2$ at high pressure have not been investigated.

In the present work, we first characterize the in-situ Raman spectra of synthetic polycrystalline Ba$_3$(PO$_4$)$_2$ and Sr$_3$(PO$_4$)$_2$ at high pressure, using a diamond-anvil cell. The pressure effects on vibrations of Ba$_3$(PO$_4$)$_2$ and Sr$_3$(PO$_4$)$_2$ are also described.

2. Experimental

High-purity samples were prepared by solid-state reactions from NH$_4$H$_2$PO$_4$ and MCO$_3$ (M = Ba and Sr). Reagent-grade NH$_4$H$_2$PO$_4$ and MCO$_3$ (M = Ba and Sr) powders were mixed...
in the proportion corresponding to the $M_3(PO_4)_2$ ($M =$ Ba and Sr) stoichiometry, and the mixture was ground sufficiently and pressed into pellets with a diameter of 5 mm under a uniaxial pressure of 30 MPa. The pellets were sintered at 1300 K for 48 h to form a single phase. The sintered product was ground finely and characterized by powder X-ray diffraction. The X-ray patterns confirmed the synthetic $Ba_3(PO_4)_2$ or $Sr_3(PO_4)_2$ is a single phase.

The high-pressure Raman measurements using a symmetric piston-cylinder type of DAC equipped with 400 μm culet diamond anvils were carried out with a customized Raman spectroscopy system. The experimental method used in this study was similar to a previous study [19]. A stainless steel plate with an initial thickness of 250 μm was used as a gasket. The central area of the gasket was pre-induced to a thickness of about 30 μm, and a hole of 150 μm in diameter was drilled at the center. The synthetic sample was loaded into the sample chamber, with the 16:3:1 methanol–ethanol–water as the pressure medium. A few ruby ($Cr^{3+}$ doped $\alpha$-Al$_2$O$_3$) chips as pressure markers were carefully placed inside the gasket sample chamber before the sample was loaded. The sample pressures were determined using the ruby fluorescence method with an accuracy of ±0.1 GPa [20]. Micro-Raman spectra were recorded in backscattering geometry using a SpectraPro Raman spectrometer from Acton with an ultra-sensitive, back-illuminated, liquid nitrogen cooled CCD detector. The resolution is better than 1 cm$^{-1}$. Excitation was achieved by adopting an argon-ion laser from Coherent Inc. with a wavelength of 488 nm and an output power of 0.350 W. The spectrometer was calibrated using a neon lamp achieving a spectral uncertainty of ±1 cm$^{-1}$. The acquisition time of each spectrum was 90 s.

3. Results and discussion

According to the factor group analysis based on the R-3m space group ($D^{15}_{3d}$), the $Ba_3(PO_4)_2$ and $Sr_3(PO_4)_2$ structures yield the same Raman active vibrations as the following:

\[ \Gamma' = 5A_{1g} + 6E_g. \]

Thus, a total of 11 Raman vibrational modes are predicted. Among these, the internal modes include two antisymmetric stretching ($A_{1g} + E_g$, $v_3$), one symmetric stretching ($A_{1g}$, $v_1$), two deformation bending ($A_{1g} + E_g$, $v_4$) and one bending vibration ($E_g$, $v_2$). The external vibrations include PO$_4$ translations ($A_{1g} + E_g$), Ba or Sr translations ($A_{1g} + E_g$) and PO$_4$ librations ($E_g$).

The Raman spectra of $Ba_3(PO_4)_2$ and $Sr_3(PO_4)_2$ at ambient conditions are shown in Fig. 2. The number of observed Raman vibrations is fewer than predicted, because of the low intensity of some external modes. In Fig. 2, six Raman active vibrations can be attributed to the phosphate internal modes. For $Ba_3(PO_4)_2$, the corresponding wavenumbers are 1043 and 980 cm$^{-1}$ for $v_1$ ($A_{1g} + E_g$), 929 cm$^{-1}$ for $v_1$ ($A_{1g}$), 601 and 563 cm$^{-1}$ for $v_4$ ($A_{1g} + E_g$), and 413 cm$^{-1}$ for $v_2$ ($E_g$). And for $Sr_3(PO_4)_2$, the corresponding wavenumbers are 1071 and 997 cm$^{-1}$ for $v_1$ ($A_{1g} + E_g$), 954 cm$^{-1}$ for $v_1$ ($A_{1g}$), 622 and 573 cm$^{-1}$ for $v_4$ ($A_{1g} + E_g$), and 418 cm$^{-1}$ for $v_2$ ($E_g$). The external modes deriving from the vibrations of PO$_4$ and Ba–O or Sr–O bonds below 400 cm$^{-1}$ were observed at 207, 166 and 113 cm$^{-1}$ for $Ba_3(PO_4)_2$, and at 244, 218, 174 and 143 cm$^{-1}$ for $Sr_3(PO_4)_2$, respectively. These vibrations agree with previous Raman characteristics of $Ba_3(PO_4)_2$ and $Sr_3(PO_4)_2$ at ambient conditions [15, 16]. The different Raman shifts between $Ba_3(PO_4)_2$ and $Sr_3(PO_4)_2$ for the same vibrations are mainly due to the interatomic distances which have been reported by previous studies [12, 13], as listed in Table 1. The corresponding interatomic distances are smaller in $Sr_3(PO_4)_2$ than those in $Ba_3(PO_4)_2$. A smaller bond length implies a stiffer or stronger bond, i.e., large force constant, and consequently higher vibrational frequency according to Hooke’s law, which is consistent with our observations in this study.

High-pressure Raman spectra of $Ba_3(PO_4)_2$ and $Sr_3(PO_4)_2$ were collected up to 30.7 GPa and 30.1 GPa, respectively. The typical Raman spectra of $Ba_3(PO_4)_2$ and $Sr_3(PO_4)_2$ at high pressures are reproduced in Fig. 3. It is obvious that, with increasing of pressure,

| Table 1 |
|-----------------|-----------------|-----------------|-----------------|
|                | $Ba_3(PO_4)_2$  |                | $Sr_3(PO_4)_2$  |                | $y$–$Ca_3(PO_4)_2$ |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| P–O(1)          | 1.542(8)        | 1.553(1)        | 1.522(6)        | 1.54(1)         | 1.526(6)         | 1.535(2)         |
| P–O(2)(×3)      | 1.549(2)        | 1.553(1)        | 1.549(2)        | 1.55(1)         | 1.526(6)         | 1.535(2)         |
the Raman peaks of Ba$_3$(PO$_4$)$_2$ and Sr$_3$(PO$_4$)$_2$ gradually shift to higher frequencies, which indicates a decreasing bond length of the phosphate tetrahedron and metal polyhedron. The spectra of Ba$_3$(PO$_4$)$_2$ and Sr$_3$(PO$_4$)$_2$ do not show any splitting or merging peaks, which indicates that no phase transformations occur in the present study.

In the present study, a methanol:ethanol:water (16:3:1) mixture was used as pressure medium, which remains hydrostatic up to 30 GPa. In order to avoid the non-hydrostatic effect, we only used the data collected below 14.4 GPa for quantitative analysis. The Raman shift versus pressure plots of Ba$_3$(PO$_4$)$_2$ and Sr$_3$(PO$_4$)$_2$ are illustrated in Fig. 4. It is noted that, due to the relatively low intensities of external vibrations of Ba$_3$(PO$_4$)$_2$ and Sr$_3$(PO$_4$)$_2$ during compression, it is difficult to determine the external modes under high pressures precisely. Therefore, the changes of internal vibrations of Ba$_3$(PO$_4$)$_2$ and Sr$_3$(PO$_4$)$_2$ at high pressures are not considered in this study. The Raman shifts of PO$_4$ internal modes in Ba$_3$(PO$_4$)$_2$ and Sr$_3$(PO$_4$)$_2$ change linearly and continuously with pressure.

The pressure coefficients ($\alpha$) of PO$_4$ modes in Ba$_3$(PO$_4$)$_2$ and Sr$_3$(PO$_4$)$_2$ (Table 2) indicate that $\nu_1$ and $\nu_1$ stretching vibrations in the high-frequency region are more sensitive to pressure compared to the $\nu_4$ and $\nu_2$ bending vibrations in the low-frequency region for the same composition. In fact, the pressure coefficients of $\nu_3$ and $\nu_1$ modes in Ba$_3$(PO$_4$)$_2$ are 2.8179–3.4186 cm$^{-1}$ GPa$^{-1}$ and 2.9609 cm$^{-1}$ GPa$^{-1}$, and in Sr$_3$(PO$_4$)$_2$ are 3.4247–4.3765 cm$^{-1}$ GPa$^{-1}$ and 3.7808 cm$^{-1}$ GPa$^{-1}$, whereas the coefficients for $\nu_4$ and $\nu_2$ modes in Ba$_3$(PO$_4$)$_2$ are 0.9855–1.8085 cm$^{-1}$ GPa$^{-1}$ and 1.4330 cm$^{-1}$ GPa$^{-1}$, and in Sr$_3$(PO$_4$)$_2$ are 1.1005–1.9244 cm$^{-1}$ GPa$^{-1}$ and 1.5647 cm$^{-1}$ GPa$^{-1}$, respectively.

In previous study, the high-pressure Raman spectra of $\gamma$-Ca$_3$(PO$_4$)$_2$, which has the same structure as Ba$_3$(PO$_4$)$_2$ and Sr$_3$(PO$_4$)$_2$, have been investigated [18]. The results are also listed in Table 2. Obviously, the wavenumbers of $\nu_0$ and pressure coefficients ($\alpha$) of corresponding PO$_4$ modes in $\gamma$-Ca$_3$(PO$_4$)$_2$ are larger than those in Ba$_3$(PO$_4$)$_2$, Sr$_3$(PO$_4$)$_2$, except the $\nu_2$ bending vibration. The differences are due to the different interatomic distances compared in Table 1. For the $\nu_2$ bending vibration in $\gamma$-Ca$_3$(PO$_4$)$_2$, other factors, such as interatomic angles, may have a large effect.

The pressure coefficients of the different Raman modes can be used to obtain the Grüneisen parameters which are required in many theoretical calculations. However, there is no information for the isothermal bulk modulus of Ba$_3$(PO$_4$)$_2$ and Sr$_3$(PO$_4$)$_2$. Hence, the mode–Grüneisen parameters cannot be calculated in this study. Based on the fact that pressure coefficients of all PO$_4$ internal modes are smaller for Ba$_3$(PO$_4$)$_2$ than Sr$_3$(PO$_4$)$_2$, we may deduce a smaller compressibility for Ba$_3$(PO$_4$)$_2$ than Sr$_3$(PO$_4$)$_2$ under high pressure.

4. Conclusions

We first measured the Raman spectra of synthetic orthophosphates Ba$_3$(PO$_4$)$_2$ and Sr$_3$(PO$_4$)$_2$ up to 30.7 GPa and 30.1 GPa, respectively. The Raman shifts of all PO$_4$ internal modes increase linearly with pressure, and no pressure-induced phase transformation occurs in present studies. The pressure coefficients of phosphate modes of Ba$_3$(PO$_4$)$_2$ and Sr$_3$(PO$_4$)$_2$ were determined, and the pressure coefficients of corresponding modes are smaller for Ba$_3$(PO$_4$)$_2$ than Sr$_3$(PO$_4$)$_2$, indicating a relative softer compressibility for Ba$_3$(PO$_4$)$_2$ than Sr$_3$(PO$_4$)$_2$.

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