High-pressure Raman spectra of Sr-substituted $\gamma$-Ca$_{3-x}$Sr$_x$(PO$_4$)$_2$

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High-pressure Raman spectra of Sr-substituted \( \gamma \)-Ca\(_{3-x}\)Sr\(_{x}\)(PO\(_4\))\(_2\)

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By using diamond anvil cell (DAC), high-pressure Raman spectroscopic studies of Sr-substituted \( \gamma \)-Ca\(_{3-x}\)Sr\(_{x}\)(PO\(_4\))\(_2\) \((x = 0.5, 1, 2)\) were carried out up to 30.7, 32.4 and 31.4 GPa, respectively. No pressure-induced phase transformation was observed in the present studies. The behaviors of the phosphate modes in \( \gamma \)-Ca\(_{3-x}\)Sr\(_{x}\)(PO\(_4\))\(_2\) \((x = 0.5, 1, 2)\) below 14.4 GPa were quantitatively analyzed since a methanol:ethanol:water \((16:3:1)\) mixture was used as the pressure medium in DAC. The Raman wavenumbers of all PO\(_4\) vibrations increased linearly and continuously with pressure for \( \gamma \)-Ca\(_{3-x}\)Sr\(_{x}\)(PO\(_4\))\(_2\) \((x = 0.5, 1, 2)\). With the increasing content of Sr, the corresponding pressure coefficients \( \alpha \) changed, and the \( \nu_{10} \) shifts to higher wavenumbers except that for \( \nu_2 \) bending vibration.

**Keywords:** \( \gamma \)-Ca\(_{3-x}\)Sr\(_{x}\)(PO\(_4\))\(_2\); Raman spectroscopy; high pressure

1. Introduction

The tricalcium phosphate (TCP, Ca\(_3\)(PO\(_4\))\(_2\)) is an important phosphate, which has four polymorphs including \( \alpha' \)-, \( \alpha \)-, \( \beta \)- and \( \gamma \)-phases. The \( \alpha' \)-, \( \alpha \)- and \( \beta \)-phases are stable from high to low temperature at ambient pressure [1–3], and the \( \gamma \)-phase is a high pressure polymorph [4,5]. The \( \gamma \)-phase was also found in Suizhou L6 chondrite and named as tuite [6], which is regarded as an important host for very large lithophile elements (such as U, Th, Ba, Sr) and rare earth elements in the lunar rock and the earth’s mantle [5–7].

The \( \gamma \)-TCP crystallizes in the rhombohedral system with the space group \( R-3m \) [7], which is the same as Sr\(_3\)(PO\(_4\))\(_2\) [8]. Compared with the calcium cation, the strontium cation has the same charge and preferred coordination geometry. In both \( \gamma \)-TCP and Sr\(_3\)(PO\(_4\))\(_2\), there are two kinds of alkaline earth cations coordinated with 10 and 12 oxygen atoms. The radius of strontium cation \((r_1 = 1.36 \, \text{Å} \text{ in coordination 10 and } 1.44 \, \text{Å} \text{ in coordination 12})\) is a little larger than that of the calcium cation \((r_1 = 1.23 \, \text{Å} \text{ in coordination 10 and } 1.34 \, \text{Å} \text{ in coordination 12})\), but the differences in the radii of cations are small (up to 10%), which allows the solid solution to form easily. Previous study showed that with the increasing content of Sr in \( \gamma \)-Ca\(_{3-x}\)Sr\(_{x}\)(PO\(_4\))\(_2\), the unite cell

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The γ-Ca3(PO4)2 and Sr3(PO4)2 have been investigated by synchrotron radiation X-ray diffraction and micro-Raman spectroscopy [10–13]. However, there is little work on the physical and chemical properties of Sr-substituted γ-Ca3−xSr2x(PO4)2 at high pressures.

The purpose of this study is to investigate the Raman spectra of synthetic γ-Ca3−xSr2x(PO4)2 (x = 0.5, 1, 2) at high pressures using diamond anvil cell (DAC). The effects of pressure and Sr substitution on vibrations of γ-Ca3−xSr2x(PO4)2 are also discussed, combined with previous results of γ-Ca3(PO4)2 and Sr3(PO4)2 [11–12].

2. Experimental

The γ-Ca3-xSr2(PO4)2 (x = 0.5, 1, 2) was synthesized at high-pressure and high-temperature conditions, as described by Zhai et al. [9]. 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 the same as that previously adopted [12]. A stainless steel plate with an initial thickness of 250 μm was used as a gasket. The central area of the gasket was pre-indent 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 (Cr3+-doped α-Al2O3) chips as the pressure marker were carefully placed inside the gasket sample chamber before the sample was loaded. The experimental pressures were determined using the ruby fluorescence method with an accuracy of ±0.1 GPa [14]. 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 Ar+ 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. The acquisition time of each spectrum was 90 s.

3. Results and discussion

The γ-Ca3−xSr2x(PO4)2 (x = 0.5, 1, 2) structural belongs to the R-3m space group with z = 3, and in this structure, a phosphorus atom is tetrahedrally coordinated by oxygen atoms and alkaline earth atoms occupy two types of large metal sites. According to the factor group analysis based on the R-3m space group (D3d), the γ-Ca3−xSr2x(PO4)2 (x = 0.5, 1, 2) structure yields the following Raman-active vibrations:

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

Thus, 11 Raman vibrational modes are predicted in total. Among these, the internal PO4 modes include two antisymmetric stretching (A1g + Eg, ν3), one symmetric stretching (A1g, ν1), two deformation bending (A1g + Eg, ν4), and one bending vibrations (Eg, ν2). The external vibrations include PO4 translations (A1g + Eg), Ca or Sr translations (A1g + Eg), and PO4 librations (Eg), which are very weak during compression. Therefore, the external vibrations are not considered in the present study.

Figure 1 shows the typical Raman spectra of γ-Ca3−xSr2x(PO4)2 (x = 0.5, 1, 2) at different pressures. All six Raman active PO4 vibrations are clearly observed at low pressure. For the sample of γ-Ca2.5Sr0.5 (PO4)2 at 0.01 GPa, the corresponding wavenumbers are 1089.4 and 1001.8 cm⁻¹ for ν3 (A1g + Eg), 971.6 cm⁻¹ for ν1 (A1g), 637.2 and 577.1 cm⁻¹ for ν4 (A1g + Eg),...
Figure 1. Representative micro-Raman spectra of $\gamma$-Ca$_{2.5}$Sr$_{0.5}$(PO$_4$)$_2$ (a), $\gamma$-Ca$_2$Sr(PO$_4$)$_2$ (b), and $\gamma$-CaSr$_2$ (PO$_4$)$_2$ (c) at different pressures.

and 414.7 cm$^{-1}$ for $\nu_2$ (E$_g$), respectively. For the sample of $\gamma$-Ca$_2$Sr(PO$_4$)$_2$ at ambient pressure, the corresponding wavenumbers are 1085.5 and 1001.3 cm$^{-1}$ for $\nu_3$ (A$_{1g}$ + E$_g$), 965.8 cm$^{-1}$ for $\nu_1$ (A$_{1g}$), 632.1 and 575.2 cm$^{-1}$ for $\nu_4$ (A$_{1g}$ + E$_g$), and 414.3 cm$^{-1}$ for $\nu_2$ (E$_g$), respectively. For the sample of $\gamma$-CaSr$_2$(PO$_4$)$_2$ at ambient pressure, the corresponding wavenumbers are 1081.5 and 1000.3 cm$^{-1}$ for $\nu_3$ (A$_{1g}$ + E$_g$), 961.0 cm$^{-1}$ for $\nu_1$ (A$_{1g}$), 626.6 and 573.7 cm$^{-1}$ for $\nu_4$ (A$_{1g}$ + E$_g$), and 415.3 cm$^{-1}$ for $\nu_2$ (E$_g$), respectively. These vibrations are consistent with previous Raman spectra of $\gamma$-Ca$_{3-x}$Sr$_x$(PO$_4$)$_2$ [9].
The Raman spectra for $\gamma$-Ca$_{2.5}$Sr$_{0.5}$(PO$_4$)$_2$, $\gamma$-Ca$_2$Sr(PO$_4$)$_2$, and $\gamma$-CaSr$_2$(PO$_4$)$_2$ were collected up to 30.7, 32.4, and 31.4 GPa, respectively. With increasing pressure, the Raman peaks of $\gamma$-Ca$_{3-x}$Sr$_x$(PO$_4$)$_2$ gradually broaden and shift to higher wavenumbers, indicating a decreasing bond length of phosphate tetrahedron. And the spectra do not show any splitting or merging peaks, indicating that $\gamma$-Ca$_{3-x}$Sr$_x$(PO$_4$)$_2$ does not exhibit any phase transformation to the highest pressure in the present studies.

In all experiments, a methanol:ethanol:water (16:3:1) mixture was used as the pressure medium, which remains hydrostatic up to 14.4 GPa at room temperature [15]. Consequently, the non-hydrostatic effect is unavoidable for the pressure range of this study (up to 30 GPa). In order to evade the non-hydrostatic effect, only the data collected below 14.4 GPa were adopted for quantitative analysis. Figure 2 presents the wavenumbers versus pressure plots for $\gamma$-Ca$_{2.5}$Sr$_{0.5}$(PO$_4$)$_2$,
γ-Ca2Sr(PO4)2, and γ-CaSr2(PO4)2. The wavenumbers of phosphate modes for γ-Ca3−xSr x(PO4)2 (x = 0.5, 1, 2) change linearly and continuously with pressures. Generally, the stretching vibrations (ν3 and ν1) are more sensitive to pressure than those of bending vibrations (ν4 and ν2) in each sample.

The pressure coefficients (α) of PO4 modes (Table 1) give quantitative comparisons for the changes of different PO4 vibrations with pressure. In fact, the pressure coefficients of ν3 and ν1 modes in γ-Ca2.5Sr0.5(PO4)2 are 3.28–4.41 and 3.38 cm−1 GPa−1, in γ-Ca2Sr(PO4)2 are 3.81–4.73 and 4.14 cm−1 GPa−1, and in γ-CaSr2(PO4)2 are 3.90–4.61 and 3.77 cm−1 GPa−1, whereas the coefficients for ν4 and ν2 modes in γ-Ca2.5Sr0.5(PO4)2 are 1.71–0.90 and 1.30 cm−1 GPa−1, in γ-Ca2Sr(PO4)2 are 2.14–1.13 and 1.57 cm−1 GPa−1, and in γ-CaSr2(PO4)2 are 2.29–1.11 and 1.52 cm−1 GPa−1, respectively. The νi0 of different PO4 modes are also listed in Table 1. Obviously,

**Table 1. Raman wavenumber shifts with pressure for γ-Ca3−xSr x(PO4)2.**

<table>
<thead>
<tr>
<th>PO4</th>
<th>γ-Ca2.5Sr0.5(PO4)2</th>
<th>γ-Ca2Sr(PO4)2</th>
<th>γ-CaSr2(PO4)2</th>
<th>γ-Ca3(PO4)2</th>
<th>Sr3(PO4)2</th>
</tr>
</thead>
<tbody>
<tr>
<td>v3</td>
<td>1088.2</td>
<td>1086.0</td>
<td>1081.2</td>
<td>1094.9</td>
<td>1071.1</td>
</tr>
<tr>
<td></td>
<td>3.28(11)</td>
<td>3.81(8)</td>
<td>3.90(13)</td>
<td>3.72(7)</td>
<td>3.42(5)</td>
</tr>
<tr>
<td>v1</td>
<td>970.2</td>
<td>966.1</td>
<td>962.3</td>
<td>978.8</td>
<td>953.4</td>
</tr>
<tr>
<td></td>
<td>3.38(14)</td>
<td>4.73(9)</td>
<td>4.61(14)</td>
<td>4.31(11)</td>
<td>3.78(6)</td>
</tr>
<tr>
<td>v4</td>
<td>636.8</td>
<td>633.3</td>
<td>626.9</td>
<td>641.6</td>
<td>622.3</td>
</tr>
<tr>
<td></td>
<td>1.71(9)</td>
<td>2.14(6)</td>
<td>2.29(12)</td>
<td>2.12(8)</td>
<td>1.92(6)</td>
</tr>
<tr>
<td>v2</td>
<td>414.0</td>
<td>575.8</td>
<td>574.6</td>
<td>576.8</td>
<td>572.8</td>
</tr>
<tr>
<td></td>
<td>1.30(6)</td>
<td>1.13(3)</td>
<td>1.11(8)</td>
<td>1.15(6)</td>
<td>1.10(3)</td>
</tr>
<tr>
<td></td>
<td>1.57(3)</td>
<td>1.52(8)</td>
<td>1.53(6)</td>
<td>1.56(6)</td>
<td></td>
</tr>
<tr>
<td>νi0</td>
<td>576.7</td>
<td>575.8</td>
<td>574.6</td>
<td>576.8</td>
<td>572.8</td>
</tr>
<tr>
<td></td>
<td>0.90(5)</td>
<td>1.13(3)</td>
<td>1.11(8)</td>
<td>1.15(6)</td>
<td>1.10(3)</td>
</tr>
</tbody>
</table>

Note: νi0 and α represent the parameters in the expression: νp = νi0 + αP, where νp and νi0 are in cm−1 and α is in cm−1 GPa−1. The data for γ-Ca3(PO4)2 and Sr3(PO4)2 were from previous studies [11–12].

Figure 3. Variations of pressure coefficients α for different vibrational PO4 modes with Sr content in γ-Ca3−xSr x(PO4)2. The data for γ-Ca3(PO4)2 and Sr3(PO4)2 were from previous studies [11–12].
the ν10 decrease with increasing contents of Sr in γ-Ca3−xSr4(PO4)2 except that for ν2 bending vibration which shows a opposite change. The results are similar to those of the previous study at ambient conditions [9].

The variations of pressure coefficients for different PO4 modes with the Sr content in γ-Ca3−xSr4(PO4)2 are illustrated in Figure 3. Obviously, the pressure coefficients of stretching PO4 vibrations (ν3 and ν1) are larger than those of bending PO4 vibrations (ν4 and ν2). It seems that there are not regular variations of pressure coefficients with Sr contents in γ-Ca3−xSr4(PO4)2. The phenomena may be related to the structural evolutions of PO4 tetrahedron in γ-Ca3−xSr4(PO4)2, which are required to be investigated.

4. Conclusions

We investigated the Raman spectra of synthetic γ-Ca3−xSr4(PO4)2 (x = 0.5, 1, 2) at 350–1200 cm−1 up to 30.7, 32.4, and 31.4 GPa, respectively. The Raman wavenumbers of all PO4 modes increase continuously and linearly with pressure, and no pressure-induced phase transformation occurs in the pressure ranges at ambient temperature. The pressure coefficients of PO4 modes of γ-Ca3−xSr4(PO4)2 were determined. For different PO4 vibrations, the pressure coefficients α change with various contents of Sr in γ-Ca3−xSr4(PO4)2.

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