High pressure Raman spectroscopic study of low-cristobalite GaPO₄

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Abstract. Gallium orthophosphate of low-cristobalite structure has been studied by Raman spectroscopy up to 28.5 GPa. Three phase transitions have been identified: 1.6, 3.1 and ~7 GPa. Raman spectra (200 to 700 cm⁻¹) acquired above 3 GPa show signs of six-coordinated gallium ions, in agreement with earlier studies that the orthorhombic \textit{C222₁} structure transforms into the orthorhombic \textit{Cmcm} structure. As pressure increases above 8 GPa, the Raman peaks associated with the low-cristobalite framework structure diminish gradually and replaced by peaks that are possibly related to isolated phosphate units. The spectra also show that the structure of the quenched sample retains that of the high-pressure phase prior to decompression.

1. Introduction

Among different materials that are isostructural to the SiO₂ polymorphs, the low-quartz type AlPO₄, GaPO₄ and their solid solutions have been extensively studied for the past two decades. The piezoelectric properties of these materials have found important industrial applications [1-3]. Numerous studies regarding to the temperature and pressure stabilities of these low-quartz homeotypes have been reported using a variety of spectroscopic [4-7] and diffraction methods [8-12]. In comparison, studies of the low-cristobalite polymorphs are not as extensive. Under ambient conditions, low-cristobalite AlPO₄ and GaPO₄ have orthorhombic lattices of space group \textit{C222₁} [13]. Temperature-induced phase transition into the cubic high-cristobalite phase [14-16], and pressure-induced phase transition into a second orthorhombic \textit{Cmcm} phase have been reported [17, 18]. The latter increases the coordination number of the trivalent cation from four to six. In tetragonal low-cristobalite SiO₂, Palmer and Finger [19] and Palmer et al. [20] reported phase transition into a monoclinic phase at ~1.5 GPa, a modest pressure relative to other phase transitions reported earlier [21]. A similar orthorhombic→monoclinic phase transition has also been proposed in a recent x-ray diffraction study [18]. In the present study, low-cristobalite GaPO₄ (abbreviated as \textit{lc-GaPO₄} hereafter) is studied by Raman spectroscopy up to 28.5 GPa for a better understanding of the details related to the reported phase transition(s).
2. Experimental Methods

High pressure Raman spectroscopic study was carried out using a Mao-Bell type diamond anvil cell, which contained a pair of type-II anvils with a culet of 500 µm. Without the use of pressure-transmitting medium, powdered \(lc\)-GaPO\(_4\) obtained from Bell Laboratories was loaded together with several ruby chips into a hole of 200 µm diameter, drilled on a stainless steel gasket (250 µm thick). Pressure was calibrated using the ruby fluorescence method. The sample was excited with the 514.5-nm radiation from an argon laser. Sample excitation and collection of Raman photons were carried out in a back-scattering geometry with a 10x long working-distance objective. Raman photons were dispersed by a Spex Triplemate spectrometer equipped with a CCD detector. To avoid sample heating, the power of the incident laser beam was kept below 15 mW. Raman spectra were calibrated using the atomic emission lines from a neon discharge lamp, and spectral resolution was 5 cm\(^{-1}\).

![Figure 1. Raman spectra (200 to 700 cm\(^{-1}\)) of \(lc\)-GaPO\(_4\) at pressures up to 28.5 GPa.](image-url)
3. Results and discussion

Between 200 and 700 cm$^{-1}$, the Raman spectra of $lc$-GaPO$_4$ at various pressures are shown in Fig. 1, and the pressure dependence of selected vibrational modes are displayed in Fig. 2. The Raman spectra of $lc$-GaPO$_4$ at ambient condition, 5.1 and 14.1 GPa agree with those reported by Robeson et al. [17] at similar pressure levels. To the best of the authors’ knowledge, the symmetries and assignments of the $lc$-GaPO$_4$ Raman peaks have yet to be studied in detail. In this report, the Raman peaks are interpreted based on a framework of corner-sharing PO$_4^{3-}$ and GaO$_4^{5+}$ tetrahedral units. The strongest Raman peak of $lc$-GaPO$_4$ is located at 391 cm$^{-1}$, which is likely attributed to stretching vibrations of the bridging O atoms ($\nu(T-O-T)$, $T = Ga$ and $P$) along the axis bisecting the Ga-O-P angle. In GaPO$_4$ of low-quartz structure, this peak is located at 458 cm$^{-1}$ [22,23]. In comparison, the $\nu(Si-O-Si)$ Raman peak in low-cristobalite and low-quartz SiO$_2$ is located ~420 [24,25] and ~465 cm$^{-1}$ [26,27], respectively. The wavenumber-pressure plots (Fig. 2) indicate phase transitions at 1.6, 3.1 and ~7 GPa, and possibly an additional transition between 14 and 17 GPa. The high-pressure phases associated with these changes are labeled in this report as I’, II, III and III’, respectively.

At ~1.6 GPa, the Raman peaks at 391 and 505 cm$^{-1}$ each becomes asymmetric with high-wavenumber shoulder peaks. The gradual increase in intensity of these shoulder peaks with pressure is possibly resulted from pressure-induced orientation disorder. In addition, a weak Raman peak appears at ~580 cm$^{-1}$ at 2.1 GPa. The phase transition at ~3 GPa is highlighted by the appearance of several weak Raman peaks between 275 and 325 cm$^{-1}$ and the disappearance of the 631 cm$^{-1}$ peak. A new peak at ~570 cm$^{-1}$ also appears close to the 580 cm$^{-1}$ peak, and their intensities increase with the applied pressure. In SiO$_2$ polymorphs with six-membered rings of corner-sharing SiO$_4$ units (cristobalite, quartz and tridymite), the Raman peaks between 750 and 800 cm$^{-1}$ are attributed largely to the motions of the Si atom [28]. Similarly, it is believed that the 631 cm$^{-1}$ peak in $lc$-GaPO$_4$ is related to motions of Ga and P atoms in the framework.

![Figure 2. Plots showing Raman wavenumbers of various vibrational modes as a function of pressure in $lc$-GaPO$_4$. Open and closed circles indicate increasing and decreasing pressures, respectively. Up to three phase transitions have been identified: 1.6, 3.1 and between 6.1 and 8.1 GPa. A possible fourth transition between 14.1 and 17.0 GPa is also indicated.](image-url)
structure. Between 6.1 and 8.1 GPa, the Raman spectra clearly indicate structural changes which have not been observed in X-ray diffraction study [18]. In the spectrum acquired at 8.1 GPa, the intensity of the 427 cm\(^{-1}\) peak weakens substantially, and two peaks at 311 and 573 cm\(^{-1}\) peak become the strongest in the spectrum. In addition, the 533 cm\(^{-1}\) peak, observed at 6.1 GPa, moves up ~20 cm\(^{-1}\) and partially overlaps with the 573 cm\(^{-1}\) peak. Above 14.1 GPa, there are fewer number of Raman peaks visible in the spectra. This might be the result of deteriorating spectral intensity, or indicate a pressure-induced phase transition (into phase III'). Among them, two peaks at 314 and 574 cm\(^{-1}\) are the most intense. No further changes in the spectral pattern are visible up to the highest pressure reached in the current study (28.5 GPa). After the sample has been quenched from 28.5 GPa to ambient condition, the Raman spectrum shows two strong peaks located at 294 and 563 cm\(^{-1}\). Extrapolation of the best-fit regression lines from 28.5 GPa to ambient condition closely matches with the wavenumbers of those two peaks, which indicates that the high-pressure phase is retained (Fig. 2).

The nature of these pressure-induced changes in the Raman spectra is yet to be fully understood. Ming et al. reported no substantial changes in the X-ray diffraction pattern and the molar volume of \(\text{lc}\)-GaPO\(_4\) between 6.1 and 8.0 GPa. The Raman spectrum of the quenched phase is also different from that of Robeson et al. [17], which indicates partial reversion of the high-pressure phase back to \(\text{lc}\)-GaPO\(_4\) after decompression from 22.0 GPa. The difference is likely resulted from different experimental conditions: hydrostatic (Ref. [17]) versus non-hydrostatic (present study) compression process. Such effects have been discussed in the high-pressure Raman study of low-quartz AlPO\(_4\) [4]. Moreover, it is interesting to point out that the Raman spectrum of \(\text{lc}\)-GaPO\(_4\) at 17.0 GPa (and above) reported in this study resembles that of low-quartz GaPO\(_4\) at 16.2 GPa [6], but with different peak positions. The authors in Ref. [6] proposed the structure of the high-pressure phase is orthorhombic with \(\text{Cmcm}\) space group, and the phase transition likely occurred at ~11 GPa.

In Fig. 2, the Raman peaks at 323 and 580 cm\(^{-1}\) observed at 28.5 GPa can be traced back to their first appearances at ~3 GPa (299 and 567 cm\(^{-1}\), respectively). Moreover, because the fading of the 631 cm\(^{-1}\) peak is believed to reflect changes in the vibrational motions of Ga and P atoms, the spectral variations at ~3 GPa likely indicate a phase transition into orthorhombic \(\text{Cmcm}\) structure (II) [18,29]. As mentioned earlier, the strongest Raman peak in \(\text{lc}\)-GaPO\(_4\) is attributed to the symmetric stretching vibrations of the bridging O atoms. The fading of this Raman peak and the simultaneous strengthening of two peaks at 311 and 573 cm\(^{-1}\) above 8.1 GPa (III and III\') might have been caused by structural rearrangement of the corner-sharing polyhedra framework. It is suspected that these two peaks are attributed to the internal vibrational modes of the PO\(_4^{3-}\) tetrahedral, suggesting that interactions between Ga and O atoms have been significantly reduced.

Acknowledgments
This work was partially supported by an NSF grant DMR-0102215.

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