Temperature Dependent Raman Studies of Pr\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} Single Crystal

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Abstract. The temperature-dependent Raman studies of Pr\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} has been performed on single crystals samples in the temperature range from 80 K to 820 K. By using polarization measurement, the vibration modes of A\textsubscript{1g}, E\textsubscript{g}, and 4T\textsubscript{2g} have been assigned on 295.9 cm\textsuperscript{-1}, 497.3 cm\textsuperscript{-1}, and 102.4 cm\textsuperscript{-1}, 309.2 cm\textsuperscript{-1}, 670.6 cm\textsuperscript{-1}, 878 cm\textsuperscript{-1}, respectively. The ambiguity vibration mode around 300 cm\textsuperscript{-1} in pyrochlore compounds can be resolved. The 380 cm\textsuperscript{-1} mode showed sharpening upon heating up from 370 K which support the present of Oxygen distortion towards vacant site.

1. Introduction
The studies of cubic pyrochlore oxides, A\textsubscript{2}B\textsubscript{2}O\textsubscript{7} with A= rare earth, and B= transition metal, have been intensively carried out for over thirty years because of the novel phenomena lies on its geometrical-frustrated systems. Raman spectroscopy has been utilized in pyrochlore compounds to investigate the oxygen sublattice’s disorder [1, 2]. The Raman vibration modes in pyrochlore are well establish as A\textsubscript{1g} + E\textsubscript{g} + 4T\textsubscript{2g}, however the assignment for the intense peak around 300 cm\textsuperscript{-1} remains unclear whether it belongs to modes A\textsubscript{1g} or T\textsubscript{2g}. Furthermore, the temperature dependent of the pyrochlore spectra above the room temperature is still missing, in particular for Pr\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}.

Here, we report the temperature dependence of polarized Raman spectra of Pr\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} ranging from 80K to 820 K. Based on the symmetry analysis and polarized spectra of for the intense peak can be resolved. Our results are consistent with the present understanding of pyrochlore spectra which strongly influenced by the local change of oxygen state. We observed an appearance of Raman mode around 380 cm\textsuperscript{-1}. The polarized measurements have been performed on single crystal of Pr\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}. For the first time, the assignment of the vibration modes is completely consistent respect to the selection rules.

2. Experimental
Single crystal of Pr\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} was synthesized by the floating zone method with a high-temperature optical image furnace equipped with four xenon arc lamps (Crystal Systems inc.) under oxygen atmosphere reported by Kimura, et.al. [3]. The as-grown crystal have a dark brown color. Polarized Raman Spectra were recorded using Bruker Raman Senterra at 850 K to 80 K temperature range with a cooling/ heating stage (Linkam TM600E Tadworth UK). A diode laser (785 nm) was used and focused with 50x microscope objective. The spectral resolution of the measurement was around 3-5 cm\textsuperscript{-1}. The
measurement were carried out after temperature stabilization with laser power of 50 mW and the scan rate of 0.1 s\(^{-1}\). The spectra were subtracted by taking into account the Bose-Einstein occupation factor and fitted with Lorentzian model. The polarization was adjusted on both the incident and scattered beam. The measurement were performed parallel (\(x(y)y\) or \(x(z)z\)) and perpendicular (\(x(y)y\) or \(x(z)z\)), along axes of [011] plane.

3. Result and Discussion

According to group theory, the Raman actives vibration for the pyrochlore with the \(Fd3m\) space group are \(A_{1g} + E_g + 4T_{2g}\) modes. Figure 1 shows the Raman spectra of \(Pr_2Zr_2O_7\) for the parallel and cross polarization configurations. The peaks at 295.9 cm\(^{-1}\) and 497.3 cm\(^{-1}\) observed using the parallel polarization are assigned for the \(A_{1g}\) and \(E_g\) vibration modes, while the peaks at 102.4 cm\(^{-1}\), 309.2 cm\(^{-1}\), 670.6 cm\(^{-1}\), and 878 cm\(^{-1}\) observed using the cross polarization are all assigned for \(T_{2g}\) vibration modes. At around 300 cm\(^{-1}\), the peak for \(A_{1g}\) and \(T_{2g}\) are clearly distinguishable using different polarization configurations. According to the symmetry analysis, the \(A_{1g}\) and \(E_g\) modes are related to the oxygen with the site symmetry of 48f, while the \(T_{2g}\) modes are related to the oxygen with site symmetry of 48f and 8a. For the parallel polarization, a broad peak near \(A_{1g}\) mode and a shoulder at \(E_g\) mode are also observed. This may due to a non uniform local distortions between \(Zr-O(48f)\)-\(Zr\) bonds which might due to the lack of occupation sites of oxygen or zirconium.

![Figure 1. Room Temperature Raman spectra of \(Pr_2Zr_2O_7\) single crystal in all polarization configuration.](image)

The temperature dependent Raman Spectra of \(Pr_2Zr_2O_7\) from 140 K to 820 K using parallel and cross polarization are displayed in Fig.2. It is noted that upon increasing temperature, the broad peak near the \(A_{1g}\) (at 380 cm\(^{-1}\)) become sharper for the parallel polarization while only the \(T_{2g}\) modes around 350 cm\(^{-1}\) persist for the cross polarization. The broadening of peaks become more pronounce above 370 K. In contrast to the temperature dependent of Bose statistic, the vibration modes of \(A_{1g}\) and \(T_{2g}\), around 300 cm\(^{-1}\), show a hardening upon decreasing temperature. This hardening is a peculiar feature which could be associated with the particular distortion of the local structure. The softening of the \(E_g\) and rest of \(T_{2g}\) modes upon decreasing temperature are consistent with the observation in other pyrochlore measurements [4,5,6]. The disappearance of the \(T_{2g}\) modes upon increasing temperature indicates that the vibrations involving \(Pr-O(8a)\)-\(Pr\) bond and \(Pr-O(48f)\)-\(Zr\) bond become weaker. This is in contrast to the emerging peak around 380 cm\(^{-1}\). Both the \(T_{2g}\) and \(A_{1g}\) can be related to the local structure around the Pr site. The oxygens around the Pr site are shown in Fig. 3.
Figure 2. Polarized Raman Spectra of Pr$_2$Zr$_2$O$_7$ single crystal as a function of temperature for (a) parallel and (b) cross polarization.

Figure 3. Schematic picture of oxygens surrounding Pr site. The O($8a$) bridge the bond between Pr-O-Pr while the O($48f$) bridge the bond between Pr-O($48f$)-Zr [7].

4. Conclusion
The polarized Raman measurements of Pr$_2$Zr$_2$O$_7$ have shown that all expected modes from group analysis can be observed. The vibration modes of $A_{1g}$, $E_g$, and $4T_{2g}$ have been assigned on 295.9 cm$^{-1}$, 497.3 cm$^{-1}$, 102.4 cm$^{-1}$, 309.2 cm$^{-1}$, 670.6 cm$^{-1}$, and 878 cm$^{-1}$ respectively. For the vibration mode around 300 cm$^{-1}$, the $A_{1g}$ mode is evidenced to have lower energy compared to the $T_{2g}$ mode which should be general for the pyrochlore systems. At high temperature, the $380$ cm$^{-1}$ mode showed hardening upon heating up from 370 K. This emerging peak Raman mode is attributed to local distortions around the Pr site.

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