

# Temperature Dependent Raman Studies of $\text{Pr}_2\text{Zr}_2\text{O}_7$ Single Crystal

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**Abstract.** The temperature-dependent Raman studies of  $\text{Pr}_2\text{Zr}_2\text{O}_7$  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  $A_{1g}$ ,  $E_g$ , and  $4T_{2g}$  have been assigned on 295.9  $\text{cm}^{-1}$ , 497.3  $\text{cm}^{-1}$ , and 102.4  $\text{cm}^{-1}$ , 309.2  $\text{cm}^{-1}$ , 670.6  $\text{cm}^{-1}$ , 878  $\text{cm}^{-1}$ , respectively. The ambiguity vibration mode around 300  $\text{cm}^{-1}$  in pyrochlore compounds can be resolved. The 380  $\text{cm}^{-1}$  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,  $A_2B_2O_7$  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  $A_{1g} + E_g + 4T_{2g}$ , however the assignment for the intense peak around 300  $\text{cm}^{-1}$  remains unclear whether it belongs to modes  $A_{1g}$  or  $T_{2g}$ . Furthermore, the temperature dependent of the pyrochlore spectra above the room temperature is still missing, in particular for  $\text{Pr}_2\text{Zr}_2\text{O}_7$ .

Here, we report the temperature dependence of polarized Raman spectra of  $\text{Pr}_2\text{Zr}_2\text{O}_7$  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  $\text{cm}^{-1}$ . The polarized measurements have been performed on single crystal of  $\text{Pr}_2\text{Zr}_2\text{O}_7$ . For the first time, the assignment of the vibration modes is completely consistent respect to the selection rules.

## 2. Experimental

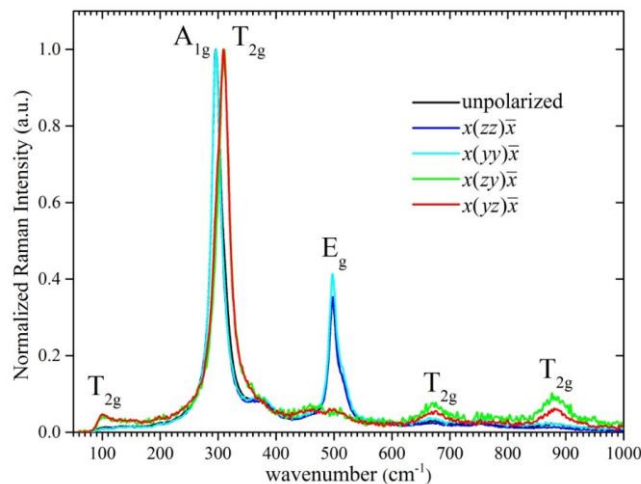
Single crystal of  $\text{Pr}_2\text{Zr}_2\text{O}_7$  was synthesized by the floating zone method with a high-temperature optical image furnace equipped with four xenon arc lamps (Crystal Systems inc.) under oxygen atmosphere reported by Kimura, et.al. [3]. The as-grown crystal have a dark brown color. 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  $\text{cm}^{-1}$ . The



measurement were carried out after temperature stabilization with laser power of 50 mW and the scan rate of  $0.1 \text{ s}^{-1}$ . 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 ( $x(\gamma\gamma)\underline{x}$  or  $x(zz)\underline{x}$ ) and perpendicular ( $x(z\gamma)\underline{x}$  or  $x(yz)\underline{x}$ ), along axes of  $[011]$  plane.

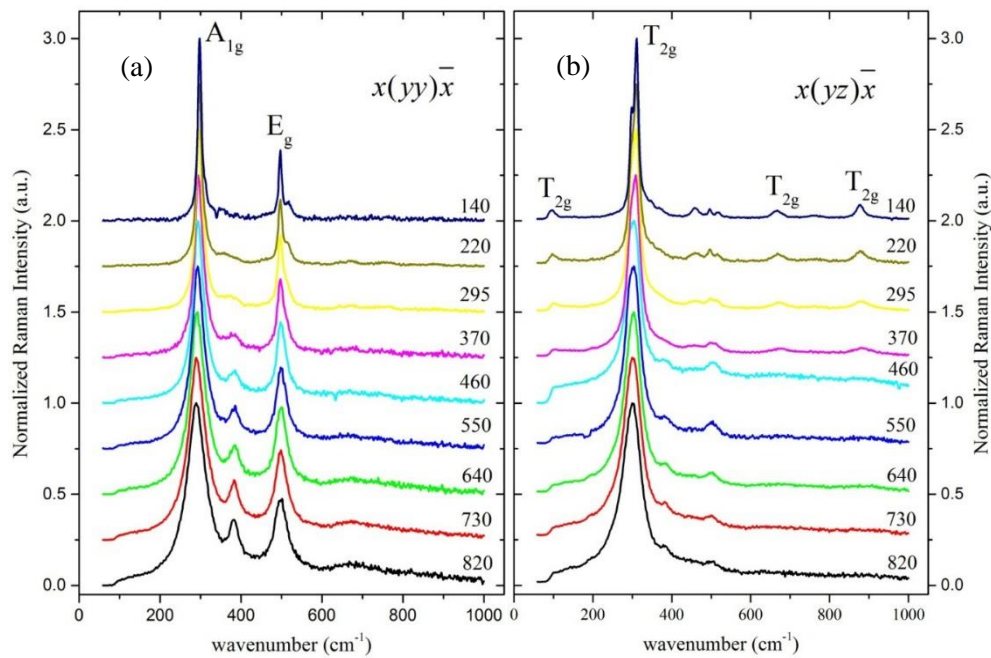
### 3. Result and Discussion

According to group theory, the Raman active vibration for the pyrochlore with the  $Fd3m$  space group are  $A_{1g} + E_g + 4T_{2g}$  modes. Figure 1 shows the Raman spectra of  $\text{Pr}_2\text{Zr}_2\text{O}_7$  for the parallel and cross polarization configurations. The peaks at  $295.9 \text{ cm}^{-1}$  and  $497.3 \text{ cm}^{-1}$  observed using the parallel polarization are assigned for the  $A_{1g}$  and  $E_g$  vibration modes, while the peaks at  $102.4 \text{ cm}^{-1}$ ,  $309.2 \text{ cm}^{-1}$ ,  $670.6 \text{ cm}^{-1}$ , and  $878 \text{ cm}^{-1}$  observed using the cross polarization are all assigned for  $T_{2g}$  vibration modes. At around  $300 \text{ cm}^{-1}$ , 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.

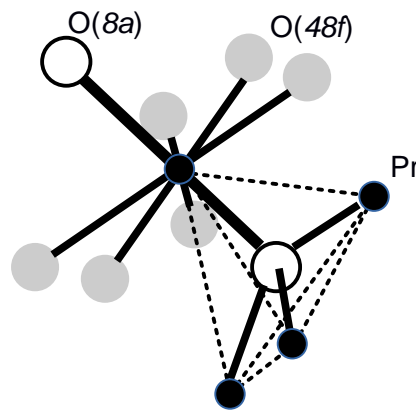


**Figure 1.** Room Temperature Raman spectra of  $\text{Pr}_2\text{Zr}_2\text{O}_7$  single crystal in all polarization configuration.

The temperature dependent Raman Spectra of  $\text{Pr}_2\text{Zr}_2\text{O}_7$  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  $380 \text{ cm}^{-1}$ ) become sharper for the parallel polarization while only the  $T_{2g}$  modes around  $350 \text{ cm}^{-1}$  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  $300 \text{ cm}^{-1}$ , 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  $380 \text{ cm}^{-1}$ . 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  $\text{Pr}_2\text{Zr}_2\text{O}_7$  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  $\text{Pr}_2\text{Zr}_2\text{O}_7$  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  $295.9\text{ cm}^{-1}$ ,  $497.3\text{ cm}^{-1}$ ,  $102.4\text{ cm}^{-1}$ ,  $309.2\text{ cm}^{-1}$ ,  $670.6\text{ cm}^{-1}$ , and  $878\text{ cm}^{-1}$  respectively. For the vibration mode around  $300\text{ cm}^{-1}$ , 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  $380\text{ cm}^{-1}$  mode showed hardening upon heating up from  $370\text{ K}$ . This emerging peak Raman mode is attributed to local distortions around the Pr site.

#### 5. Acknowledgement

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