

High Pressure Raman Scattering study on $\text{BaZr}(\text{PO}_4)_2$

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Keywords: high pressure, raman scattering, phase transition.

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Extensive physical properties like ionic conductivity, catalytic activities, radiation durability, etc, makes the family of orthophosphates an interesting research problem and they find great importance in various technological applications. Family of phosphates, $\text{AZr}(\text{PO}_4)_2$ with $A = \text{Ca}, \text{Sr}$ and Ba can be used for chemical separation of nuclear waste [1,2]. Many studies have reported structural instability of orthophosphates under extreme conditions of pressure and temperature. Barium zirconium diorthophosphate [$\text{BaZr}(\text{PO}_4)_2$] is an anhydrous ceramic compound, which has been reported to exhibit anisotropic thermal expansion[3]. $\text{BaZr}(\text{PO}_4)_2$ crystallizes in (C2/m) yavapaiite structure at ambient conditions and is reported to undergo a reversible structural transition at high temperature i.e. around 730K, to a trigonal phase[4].

When a material is subjected to high pressures, it can substantially change its structure which in turn will affect the physical properties of the material. Keeping in view the diverse structural behaviour of this family of orthophosphates, high pressure behavior of $\text{BaZr}(\text{PO}_4)_2$ has been investigated using Raman spectroscopy.

High pressure Raman scattering measurements were performed on triple stage confocal micro Raman spectrograph, where the scattered Raman signals were collected at backscattering geometry using 20x objective. Raman spectra were recorded from 100-1300 cm^{-1} . The experiments were performed using Mao-Bell type DAC with $\sim 400 \mu\text{m}$ culet size and a 488 nm argon ion laser was used as excitation source. Sample was loaded in a tungsten gasket hole of $\sim 120 \mu\text{m}$ diameter, drilled after pre-indenting it to a thickness of $\sim 50 \mu\text{m}$. Methanol-Ethanol mixture in 4:1 ratio was used as pressure transmitting medium (PTM). The pressure inside the diamond anvil cell (DAC) was monitored using well known Ruby fluorescence shift.

High pressure Raman scattering experiments reveals the ambient structure to be stable only upto ~ 1 GPa. Above this pressure, Raman spectrum shows emergence of many new Raman modes, indicating a first order structural phase transition. The Raman modes observed above the spectral range 300 cm^{-1} arise due to the internal vibrations of PO_4 tetrahedra. Splitting of internal PO_4 modes are observed around ~ 1 GPa, which indicates a structural transition to a lower symmetry phase. The first high pressure phase (HP-1) coexists with the ambient phase. With further increase in pressure, ambient structure slowly diminishes and the intensity of Raman modes from high pressure phase (HP-1) gradually increases. However, before the transition is completed, changes in the Raman spectrum are observed at ~ 3 GPa. This indicates onset of second phase transition. When

pressure is gradually increased, this new high pressure phase (HP-2) becomes prominent. At ~ 4 GPa, sample completely transforms to the HP-2 phase. This new phase remains stable upto the highest pressure in the experiments i.e. up to ~ 16 GPa. Splitting of some Raman modes are visible around ~ 7 GPa. This could be attributed to lifting of degeneracy. However, there are no significant changes in the spectrum when pressure is increased.

When pressure is slowly released, sample transforms to HP-1 phase around ~ 1 GPa and reverts to the ambient phase at complete release of pressure. However, sample shows traces of HP-1 phase at complete release of pressure.

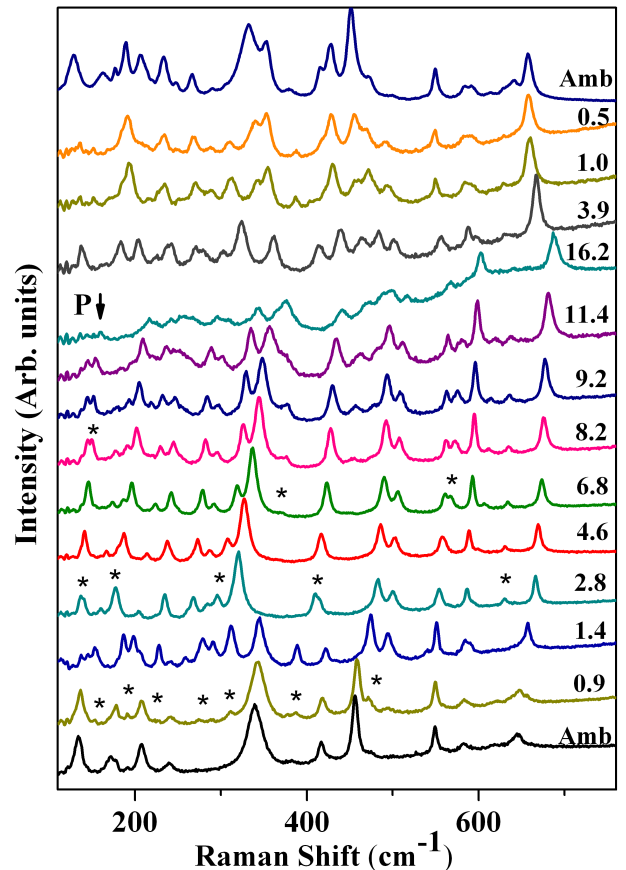


Figure 1(a). A few representative high pressure Raman Spectra of $\text{BaZr}(\text{PO}_4)_2$ up to 16 GPa. 100-800 cm^{-1}

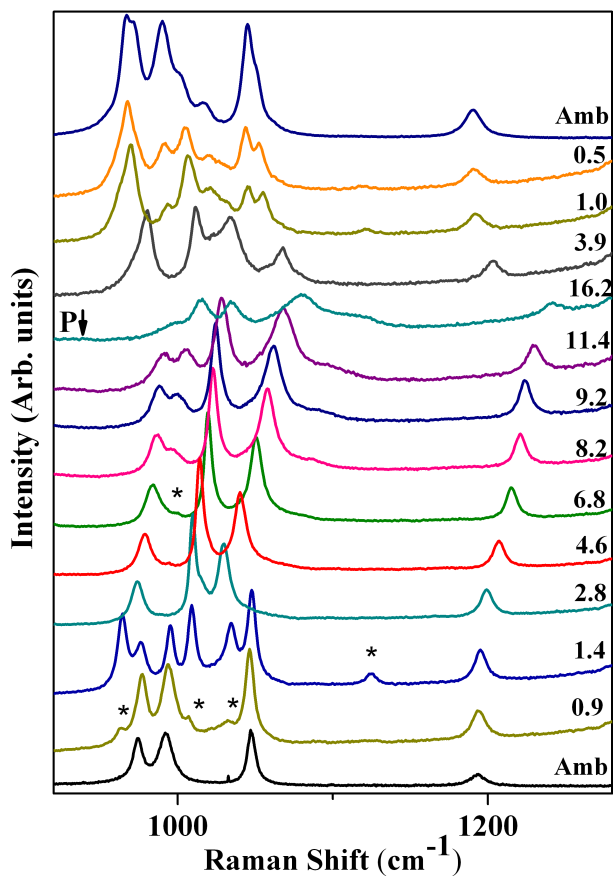


Figure 1(b). A few representative high pressure Raman Spectra of $\text{BaZr}(\text{PO}_4)_2$ up to 16 GPa. $800\text{-}1250\text{ cm}^{-1}$

Figure 1 (a) and 1 (b) shows high pressure Raman spectra of $\text{BaZr}(\text{PO}_4)_2$. Pressure mentioned at the right corner of each spectrum is in GPa scale. Pressure increase cycle starts from bottom in the upward direction. P↓ indicates onset of pressure release cycle.

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