

## Pressure Induced Structural Stabilization of Bismuth Vanadium Oxides Nanocrystals

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**Abstract:** The nanocrystalline bismuth vanadium oxides are synthesized by mechanochemical activation method. The structural stability of the nanocrystalline aurivillius oxides  $\text{Bi}_2\text{VO}_{5.5}$  and  $\text{Bi}_2\text{VO}_5$  is studied by high pressure Raman Studies and EDXRD upto 15 GPa. The phase transition is irreversible on release of pressure.

**Key words:** Oxides • Crystal Structure • Nanoparticles • Mechanochemical method • EDXRD • Raman • High Pressure • Diamond Anvil Cell

### INTRODUCTION

The family of bismuth compounds posses layered perovskite structure are named as Aurivillius oxides [1]. In recent years these family of oxides obtained large amount of attention due to their physical and structural properties. The oxide crystal structures consists of  $\text{Bi}_2\text{O}_2$  layers intercleaved with 'n' perovskite layers of  $\text{A}_{n+1}\text{BnO}_{3n+1}$ , where A-metal ion with 12 coordination number like Ba, Sr, Bi and B – metal ion with 6 coordination number like Ti, Nb, Ta, V, Mo [2]. Among the family of aurivillius the oxygen deficient structures of  $\text{Bi}_2\text{VO}_{5.5}$  and  $\text{Bi}_2\text{VO}_5$  [3, 4] are of great technological importance and they show good ionic property and are useful ferroelectric polar materials.

The bismuth – vanadium oxides are complex and have considerable importance in various fields such as catalysts, photocatalysts [5], gas sensors, solid state electrolyte [6], thermistors, positive temperature coefficient resistor (PCTR) [7], batteries [6], implantable cardiac defibrillators [8]. Recently there has been growing interest in organic pollutant removal [9, 10] and as photo-anode for photochemical water splitting [11, 12]. But their most promising ferroelectric properties are restricted due to their large dielectric losses. In order to overcome the loss the properties are improved by doping these oxides with different composition [13]. These vanadium based bismuth oxides exhibit three polymorphic phase  $\alpha$ ,  $\beta$  and  $\gamma$  at different temperature [14, 15] and show hysteresis on thermal cycle. The phase transition is reversible on cooling for  $\text{Bi}_2\text{VO}_{5.5}$  whereas they are irreversible for  $\text{Bi}_2\text{VO}_5$ . Among  $\alpha$ ,  $\beta$ ,  $\gamma$  phases the  $\gamma$  polymorphic phase of  $\text{Bi}_2\text{VO}_{5.5}$  and fluorite phase of  $\text{Bi}_2\text{VO}_5$  exhibit high ionic conductivity. A numerous

efforts have been put forth in order to stabilize the stable phases at room temperature. All conventional ceramics synthesis method, substitutional solid solution needs long reaction time and very high temperatures. This leads to degradation of the physical properties (ie) ionic conductivity. To overcome the above difficulties it is necessary to explore alternative synthesis routes which can prevent changes in stoichiometry, stability and reduce reaction time and temperatures. Mechanochemical activation method is able to fulfil these demands. It enhances the kinetics of synthesis and pave way to synthesis new materials [16-18] with uniform size distribution resulting improved physicochemical characteristics [19, 20]. Using this method nanocrystalline  $\text{Bi}_2\text{VO}_{5.5}$  and  $\text{Bi}_2\text{VO}_5$  are synthesized. The milled powders are characterized by XRD, EDS, TEM and SEM (21). The oxides are amorphous in nature with particle size 100 – 200nm and 500nm.

In the present work these oxides are subjected to high pressure upto 15GPa. The structural stability of these oxides is investigated by using EDXRD pattern and Raman spectra. The results obtained are reported and discussed.

### Experimental Procedure

**High Pressure EDXRD Set Up:** The high pressure powder X-ray diffraction experiments are performed using the Mao-Bell Diamond anvil cell which is mounted on the Rigaku 12 kW hole diameter is 300 m. The sample is placed in the hole along with methanol- ethanol (4:1) pressure transmitting medium. The pressure is applied slowly. The experiment is carried out at room temperature. The sample is pressurized to various pressures up to 15 GPa. The detector angle is fixed to  $2\theta = 16$ .

### Experimental Set-up for High Pressure Raman Studies:

The high pressure Raman studies are carried out using the diamond anvil cell (Dia cell). The diamond anvils are 600  $\mu\text{m}$  in culet face diameter. A steel gasket of thickness 300  $\mu\text{m}$  is used as the sample holder. The sample hole diameter is 300  $\mu\text{m}$ . A very small amount of ruby powder is used for the pressure determination. Care is taken to spread the ruby powder uniformly over the sample. The ethanol is used as the pressure transmitting medium. The pressure is applied gradually during loading and released slowly during unloading. The Renishaw Raman spectrometer is used for recording the Raman spectrums. The 514 nm line of the Argon ion laser with a power of 100 mW is used. Raman spectrum is obtained for both loading and unloading pressures [22].

### RESULTS AND DISCUSSION

According to literature the family of Aurivillius oxides have layered perovskite structure. The vanadium based bismuth oxides  $\text{Bi}_2\text{VO}_{5.5}$  and  $\text{Bi}_2\text{VO}_5$  have a defective two dimensional structure [23]. These oxides in bulk form crystallize in the oxygen deficient orthorhombic 2+ Rotating anode X-ray generator with energy dispersive X-ray diffraction system as explained [22]. The face diameter of the diamond anvil is 600 m. The samples are placed in between the diamonds with the help of a stainless steel plate of grade T 301 which acts as gasket and the sample structure with covalent network of  $\text{Bi}_2\text{O}_2$  between the two dimensional perovskite slabs at normal conditions [15]. The ordering of the oxygen vacancies in these slabs makes difference in the properties and performance between three polymorphic  $\alpha$ ,  $\beta$  and  $\gamma$  phase of  $\text{Bi}_2\text{VO}_{5.5}$  and  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $f$  phase of  $\text{Bi}_2\text{VO}_5$ . The oxygen deficient unstable structure of  $\text{Bi}_2\text{VO}_{5.5}$  and  $\text{Bi}_2\text{VO}_5$  can be deploying to form stable structure during mechanical treatment. When the materials are comminuted the size of the crystallites reduced, the crystal structures get damaged and provide stabilized metastable phase. But thus prepared materials are amorphous materials or nanocrystals whose structure cannot be predicted by XRD. The amorphous nature of these nanocrystalline oxides are confirmed by EDXRD pattern at ambient pressure and temperature. Fig. 1 shows EDXRD pattern of  $\text{Bi}_2\text{VO}_{5.5}$  and  $\text{Bi}_2\text{VO}_5$  at normal pressure and temperature. Only the fluorescence peaks of Bismuth and Vanadium are obtained. This confirms that the oxides are in amorphous nature before application of pressure.

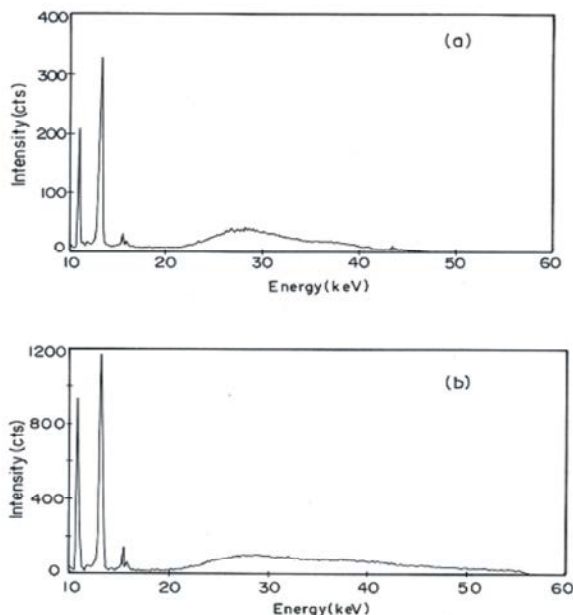


Fig. 1: EDXRD pattern of (a)  $\text{Bi}_2\text{VO}_{5.5}$  and (b)  $\text{Bi}_2\text{VO}_5$  at ambient pressure and temperature

Amorphous materials are unstable thermodynamically. Due to thermal annealing or pressurizing the amorphous phase crystallizes into stable phase. On application of pressure the interatomic spacing is reduced and small peaks emerges indicate the formation crystalline phase. According to literature, the fluorite crystalline phase of  $\text{Bi}_2\text{VO}_5$  has been indexed assuming cubic symmetry with space group  $\text{Fm}\bar{3}\text{m}$  and unit cell parameter  $a = 5.5456 \text{ \AA}$  [24] and hence the new peaks of the nano-phase oxides are also indexed to cubic structure. According to Angle Dispersive X-ray diffraction (ADXRD) pattern given in the literature, the structure of these oxides are found to be cubic. About 5-7 GPa peaks are monitored indicating the crystalline phase of these oxides. The peaks are indexed to a cubic system and the lattice parameter ( $a$ ) is found to be 5.588  $\text{\AA}$  and 5.568  $\text{\AA}$  for  $\text{Bi}_2\text{VO}_{5.5}$  and  $\text{Bi}_2\text{VO}_5$  respectively. The volume ( $V$ ) is calculated as 174.520  $\text{\AA}^3$  for  $\text{Bi}_2\text{VO}_{5.5}$  at 5.2 GPa and 172.673  $\text{\AA}^3$  for  $\text{Bi}_2\text{VO}_5$  at 4 GPa. It is found that both the lattice constant and the volume decreases as the pressure increases and the experiment is carried out up to a pressure of 15 GPa. Figures 2a and 2b shows the EDXRD pattern obtained for both the oxides at different pressure at room temperature. As the pressure increases the volume decreases and thereby decreases the bulk modulus at higher pressures.

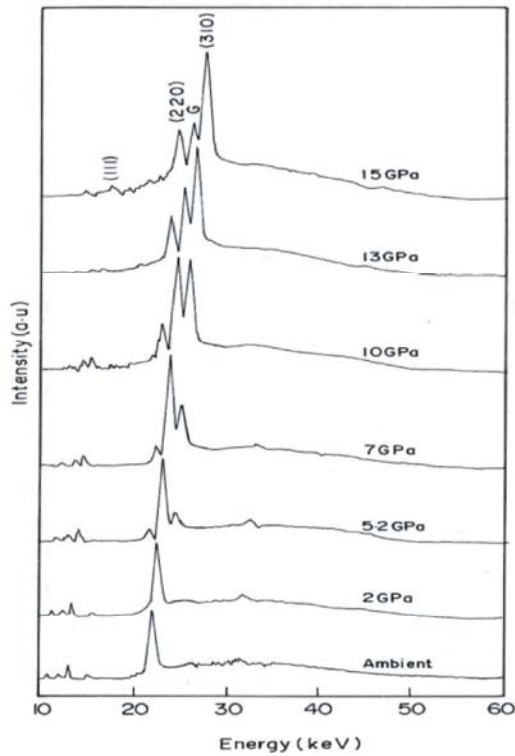


Fig. 2a: EDXRD spectra of  $\text{Bi}_2\text{VO}_5$  at different pressures

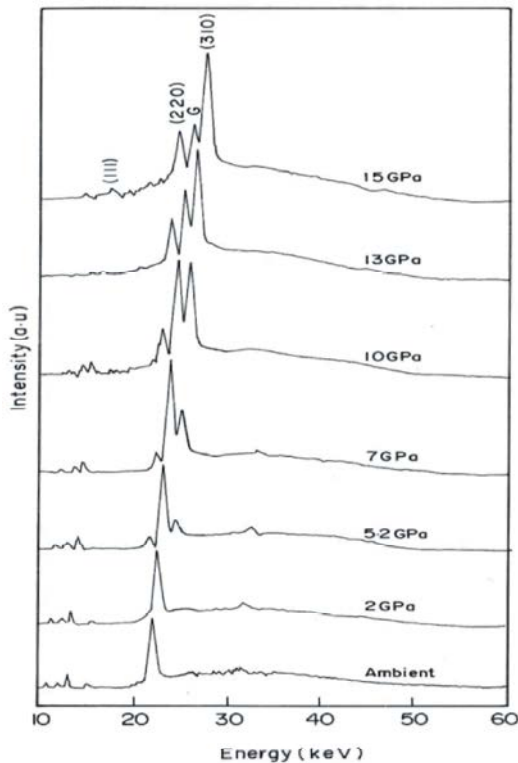


Fig. 2b: EDXRD pattern of nano  $\text{Bi}_2\text{VO}_{5.5}$  at various pressures

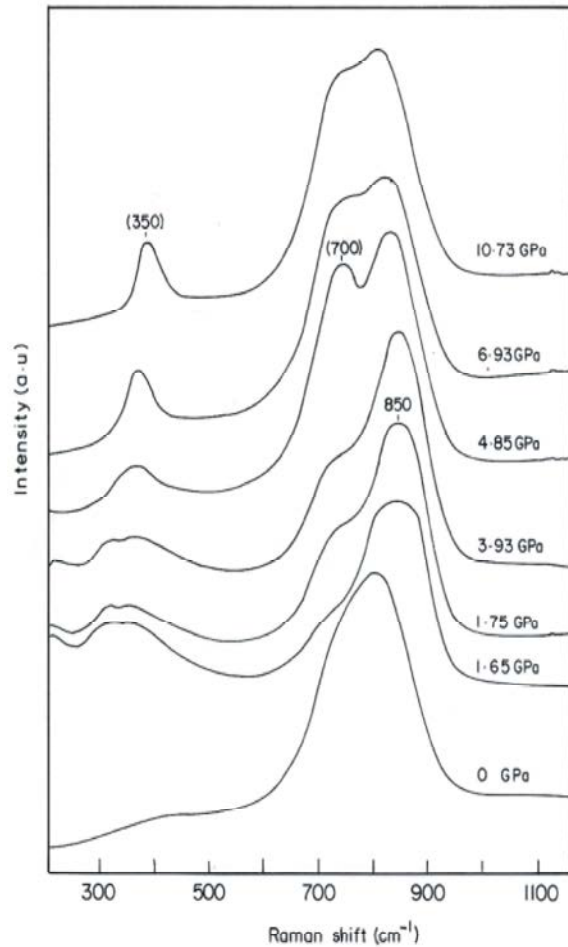


Fig. 3a: Raman Spectra of nano  $\text{Bi}_2\text{VO}_{5.5}$  at high pressure

Figures 3a and 3b Raman spectrum of  $\text{Bi}_2\text{VO}_{5.5}$  and  $\text{Bi}_2\text{VO}_5$  respectively at high pressure. From the figure it is clear that a broadened peak obtained at low pressure indicates the amorphous nature of the oxides. As the pressure is increased few peaks are monitored. The onset of transition from amorphous to crystalline starts at 8.5 Gpa for  $\text{Bi}_2\text{VO}_5$  and 4.85 GPa for  $\text{Bi}_2\text{VO}_{5.5}$  and as the pressure increases the peaks are prominent and shows a shift in the peaks position. The shift is caused due to the effect of pressure exerted on the sample. It is in agreement with the results of the high pressure EDXRD.

Byeon and co-workers reported that a layered perovskite structure directly transforms into a non-defective three dimensional perovskite at high pressure [25]. For this transformation there is no need of reducible cations in the layered precursor but the increase in anion vacancies in the precursor layered block [26].

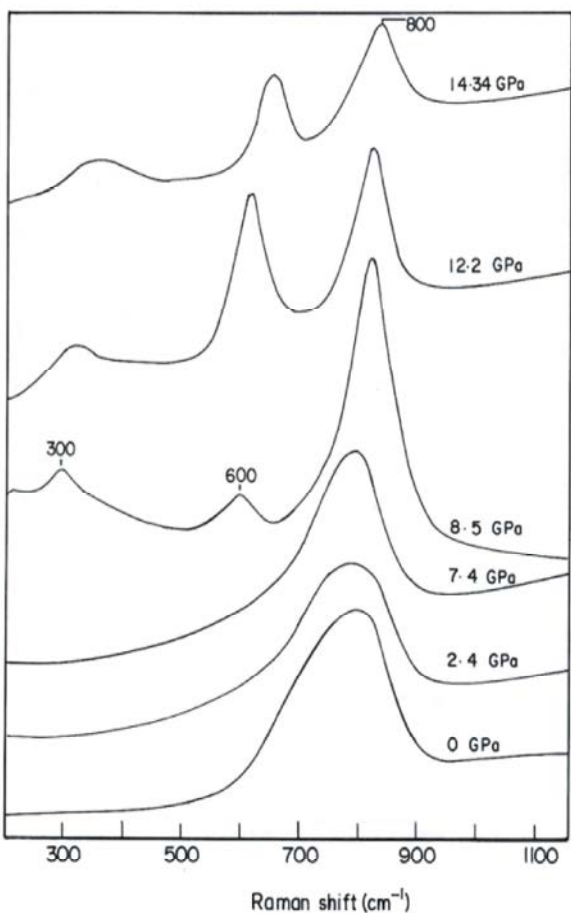


Fig. 3b: Raman Spectra of nano –  $\text{Bi}_2\text{VO}_5$  at elevated pressures

The close packed  $\text{AO}_3$  layers tend to form a stable cubic by changing the octahedral  $\text{BO}_6$  where A is the larger cation and B is a smaller cation. When the size of the A cation is too large the cubic stacking change to hexagonal sequence. Under high pressure the hexagonal sequence can be changed to perovskite structures. This structural property is important for its ferroelectric property. Moreover the defective layered structure transforms into non defective cubic stacking with no vacancy at higher pressure. This leads to the irreversible state of the oxides from crystalline to amorphous phase on release of pressure.

### CONCLUSION

The  $\text{Bi}_2\text{VO}_{5.5}$  and  $\text{Bi}_2\text{VO}_5$  prepared by mechanochemical method are amorphous in nature. On application of pressure, phase transition occurs from amorphous to crystalline phase at 5–7 GPa respectively.

The peaks emerged confirm the crystalline phase of these oxides and the transition is irreversible and remains unaltered on release of pressure. The resulted stable cubic phase of  $\text{Bi}_2\text{VO}_{5.5}$  and  $\text{Bi}_2\text{VO}_5$  provides high ionic property and ferroelectric properties can be enhanced. These aurivillius oxide can be a promising candidate for renewable energy storage devices.

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