

Synthesis, electrical and thermal properties of  $\text{Bi}_4\text{V}_{2-x}\text{Zr}_x\text{O}_{11}$  ( $x=0.0$  and  $0.06$ ) ceramics

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**ABSTRACT**

Polycrystalline ceramic samples of pure and  $\text{Zr}^{+4}$  doped  $\text{Bi}_4\text{V}_{2-x}\text{Zr}_x\text{O}_{11}$  ( $x=0.0$  and  $0.06$ ) have been synthesized by standard solid state reaction method using high purity oxides. The dielectric constant and dielectric loss and hence ac conductivity as a function of frequency and temperature have been measured. The dielectric studies indicate that the material is highly lossy and hence its ac conductivity increases with the increase of temperature. The dc conductivity of material has been measured as a function of temperature from room temperature to 653 K and its activation energy was calculated using the relation  $\sigma = \sigma_0 \exp(-E_a/kT)$ . The Modulated Differential Scanning Calorimetry (MDSC) has been used to investigate the effect of substitution on the phase transition of the compounds.

*Keywords:* Ferroelectrics, X-ray diffraction, Dielectrics, Electrical Conductivity, MDSC

**INTRODUCTION**

Bismuth vanadate  $\text{Bi}_4\text{V}_2\text{O}_{11}$  is a member of the Aurivillius homologous series  $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})^{2-}$  with  $n=1$ . Due to its strong polar response and high ionic conductivity it shows wide applications in catalysts, gas sensors, solid state electrolytes, fuel cells and oxygen pumps.  $\text{Bi}_4\text{V}_2\text{O}_{11}$  abbreviated as (BIVOX) and its substituted compound abbreviated as BIMEVOX, where ME is an n-charged cation ( $n=2-6$ ) such as Cu, Co, Al, Cr, As and Ti, were prepared mostly in ceramic form by sol-gel, modified sol-gel, co-precipitation, mechanical activation, combustion, molten salt and solid state reaction methods.<sup>1-5</sup>  $\text{Bi}_4\text{V}_2\text{O}_{11}$  compound has three structural modifications; the  $\alpha$ - $\text{Bi}_4\text{V}_2\text{O}_{11}$  was found in monoclinic crystal structure with space group C2/m and in orthorhombic crystal structure with space group P22121,  $\beta$ -form is having the orthorhombic structure in the centrosymmetric space group Amam and the  $\gamma$ -form is tetragonal with space group I4/mmm.<sup>6-8</sup> The phase transition for  $\text{Bi}_4\text{V}_2\text{O}_{11}$  occurs from  $\alpha$  to  $\beta$  at 720K,  $\beta$  to  $\gamma$  at 840 K, and  $\gamma$  to  $\gamma'$  at 1150 K while  $\gamma'$  to liquid is at 1160 K.<sup>9-10</sup> Differential

Scanning Calorimetry (DSC) studies show two endothermic peaks at 726 K and 793 K. These transitions are due to  $\alpha$  to  $\beta$  and  $\beta$  to  $\gamma$  phase changes.<sup>11</sup> Dielectric studies on nano crystalline  $\text{Bi}_4\text{V}_2\text{O}_{11}$  powders indicate that the ferroelectric to paraelectric phase transition is strongly frequency dependent.<sup>12-14</sup> The Curie-Weiss law is valid above the transition temperature. The electrical conductivity of BIVOX and BIMEVOX has been reported.<sup>15-16</sup> The present paper reports on the synthesis, electrical and thermal properties of pure and 3% Zr-doped  $\text{Bi}_4\text{V}_2\text{O}_{11}$  compounds.

**EXPERIMENTAL**

Polycrystalline ceramic samples of  $\text{Bi}_4\text{V}_{2-x}\text{Zr}_x\text{O}_{11}$  ( $x=0.0$  and  $0.06$ ) were prepared by the conventional solid state reaction method. The stoichiometric amount of  $\text{Bi}_2\text{O}_3$  (99.99%),  $\text{V}_2\text{O}_5$  (99.0%) and  $\text{ZrO}_2$  (99.9% pure) were mixed thoroughly in the liquid medium (Aceton) and calcined at 600 °C for 6 h in silica crucible in air atmosphere. The process of firing and grinding was repeated for a number of times. The resulting mixture was compressed into pellet form by applying pressure around 5 tones/cm<sup>2</sup> in a hydraulic press. These pellets were sintered at 800 °C for 2 h and 1 h respectively. The formation of the compounds was checked by X-ray diffraction pattern using Rigaku X ray diffractometer with  $\text{CuK}\alpha$  radiation in  $2\theta$  range from 15° to 90°. The instrument was calibrated using pure silicon sample provided with the instrument. The dielectric constant and dissipation factor as well as ac conductivity were measured as a function of frequency (100Hz-2MHz) and temperature (RT-673 K) using Hioki 3532-50 LCR Hitester. The dc electrical conductivity measurement was carried out using laboratory made set up from room temperature to 653 K in air atmosphere. The MDSC measurement was carried out with TA instruments Model 2910 modulated differential scanning calorimeter from

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RT to 600 °C in inert (N<sub>2</sub>) atmosphere with a heating rate of 5° C/min with ±0.75 °C modulation per 60sec.

## RESULTS AND DISCUSSION

Figure 1 shows the room temperature (RT) X-ray diffraction patterns of Bi<sub>4</sub>V<sub>2-x</sub>Zr<sub>x</sub>O<sub>11</sub> (x=0.0 and 0.06) compounds. All the peaks in both the pure and substituted compound are well matching with orthorhombic symmetry in α phase and hence these compounds show same crystal structure.<sup>7,17</sup> The temperature variation of ε' for Bi<sub>4</sub>V<sub>2-x</sub>Zr<sub>x</sub>O<sub>11</sub> (x=0.0 and 0.06) at a frequency of 100 kHz is shown in Figure 2. From the figure it is observed that ε' of x=0.0 compound increases with the increase of temperature and doesn't show any dielectric anomaly up to the measured temperature range. But ε' of Zr-doped compound with x=0.06 shows an anomaly around 583 K and then decreases rapidly. Further the peak value of ε' for x=0.06 is low (~143) which may be due to the increase in the grain size with the addition of Zr on vanadium site.<sup>18</sup>

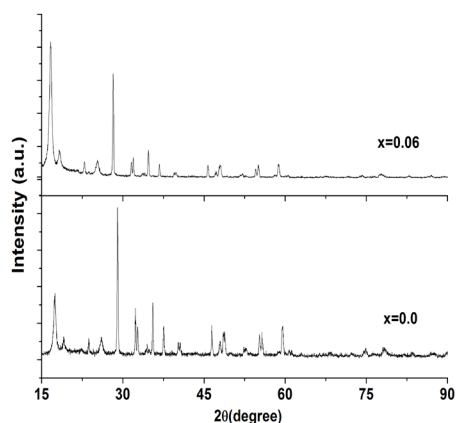


Figure 1. RT X-ray diffraction patterns of Bi<sub>4</sub>V<sub>2-x</sub>Zr<sub>x</sub>O<sub>11</sub> (x=0.0 and x=0.06).

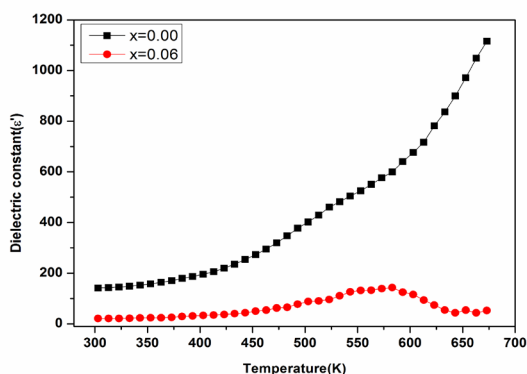


Figure 2 Dielectric constant vs temperature curves of Bi<sub>4</sub>V<sub>2-x</sub>Zr<sub>x</sub>O<sub>11</sub> (x=0.0 and 0.06) at a frequency of 100kHz.

The temperature dependence of dc conductivity (σ<sub>dc</sub>) for Bi<sub>4</sub>V<sub>2-x</sub>Zr<sub>x</sub>O<sub>11</sub> is shown in Figure 3. From the figure it is found that the conductivity increases with increase in temperature. The results suggest that the conductivity is a consequence of

thermally activated process, which can be described by the Arrhenius relation

$$\sigma = \sigma_0 \exp(-E_a/kT) \quad \text{-----} \quad (1)$$

where σ<sub>0</sub> is the pre exponential factor

E<sub>a</sub> is the activation energy of the sample which was calculated from the slope of the logσ<sub>dc</sub> versus 1000/T curve

K is Boltzman constant

T is the absolute temperature

The calculated values of activation energies are shown in table-1. From the table it is observed that the activation energy decreases with the 3 mass % substitution of Zr on vanadium site.

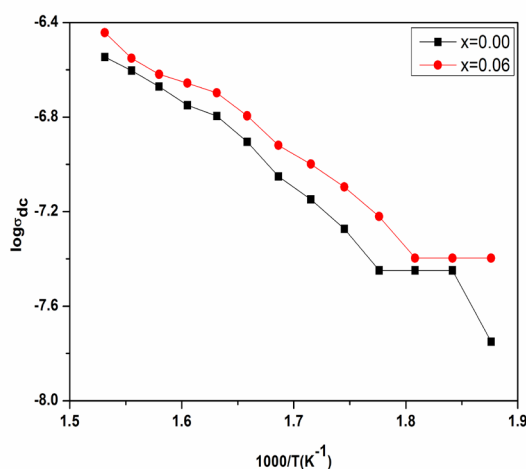


Figure 3 logσ<sub>dc</sub> vs 1000/T curves of Bi<sub>4</sub>V<sub>2-x</sub>Zr<sub>x</sub>O<sub>11</sub> (x=0.0 and 0.06).

Figure 4 shows the MDSC curves of Bi<sub>4</sub>V<sub>2</sub>O<sub>11</sub> as a function of temperature. The heat capacity curve shows exothermic peaks at 440 °C and 518 °C and the heat flow curve shows endothermic peak at 440 °C and 513 °C. However the second peak at around 515 °C in both the curves are broader than first peak at 440 °C which indicates that the second transition is sluggish. These transitions are due to α→β and β→γ phase changes. Figure 5 shows the MDSC curves of Bi<sub>4</sub>V<sub>2-x</sub>Zr<sub>x</sub>O<sub>11</sub> where x=0.06. Here the heat capacity curve shows two exothermic peaks representing α→β and β→γ phase transitions around 389 and 526 °C where as the heat flow curve shows two endothermic peaks around 383 and 526 °C. Here both α→β and β→γ transition temperatures are shifting in both the heat capacity and heat flow curves. If we compare the transition behavior of Zr-doped and pure Bi<sub>4</sub>V<sub>2</sub>O<sub>11</sub> compound then it is observed that α→β transition shifted from 440 °C in the pure compound to 389 °C (lower side) and 383 °C in the Zr-doped compound and β→γ transition shifted from 518 °C in the pure compound to 526 °C (higher side) in the Zr-doped compound. The shifting of α→β transition towards lower side and β→γ transition towards higher side may be due to the difference in ionic size of both vanadium and zirconium as well the thermal characteristics of Zr-taking the vanadium lattice site.

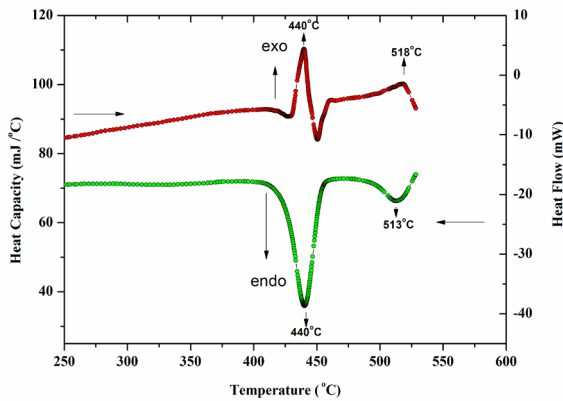


Figure 4. MDSC curves for  $\text{Bi}_4\text{V}_2\text{O}_{11}$ .

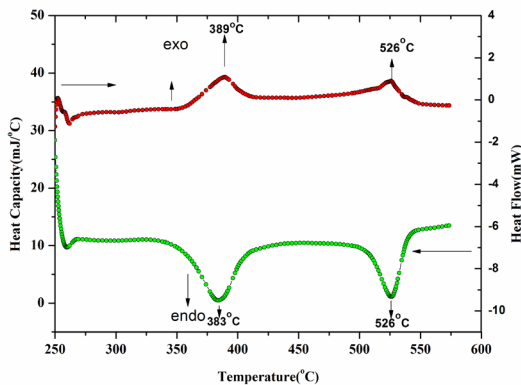


Figure 5 MDSC curves for  $\text{Bi}_4\text{V}_{1.94}\text{Zr}_{0.06}\text{O}_{11}$ .

Table-1: Physical and electrical parameters of  $\text{Bi}_4\text{V}_{2-x}\text{Zr}_x\text{O}_{11}$  ( $x=0.0$  and  $0.06$ ) ceramics

Parameter	$\text{Bi}_4\text{V}_2\text{O}_{11}$	$\text{Bi}_4\text{V}_{1.94}\text{Zr}_{0.06}\text{O}_{11}$
Grain size	18 $\mu\text{m}$	6 $\mu\text{m}$
$\alpha \rightarrow \beta$ (Tc)	440 °C	518 °C
$\beta \rightarrow \gamma$ (Tc)	389 °C	526 °C
DC activation energy	E=1.85 eV	E=1.64 eV

## CONCLUSION

In conclusion, the substitution of Zr-ions on V-site in  $\text{Bi}_4\text{V}_{2-x}\text{Zr}_x\text{O}_{11}$ , decreases the dielectric constant and increases the ac conductivity of the compound. The dc conductivity also increases slightly for Zr-doped compound. The thermal behaviour of the pure and doped compounds have been studied using MDSC technique. From this study it is concluded that the  $\alpha \rightarrow \beta$  transition and  $\beta \rightarrow \gamma$  transition

temperatures are shifting towards lower and higher sides with respect to the pure compound which depends upon the thermal characteristics of Zr present on the vanadium lattice sites.

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