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Synthesis, electrical and thermal properties of $Bi_4V_{2-x}Cu_xO_{11}$ (x=0.0 and 0.02) ceramics

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ABSTRACT

Polycrystalline ceramic samples of pure and Cu^{+2} doped $Bi_4V_{2-x}Cu_xO_{11}(x=0.0 \text{ and } 0.02)$ 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 $\sigma = \sigma_0 exp$ (-Ea/kT). The dc conductivity increases with the substitution of Cu on the vanadium site. The Modulated Differential Scanning Calorimetry (MDSC) has been used to investigate the effect of substitution on the phase transition of the compounds. The results are discussed in detail. Copyright © 2014 VBRI press.

Keywords: Ferroelectrics; X-ray diffraction; dielectrics; electrical conductivity; MDSC.



M. Roy received his Master degree from Bihar University, Muzaffarpur in 1983 and Ph. D. Degree on ferroelectric materials from IIT Kharragpur in the broad field of Experimental Solid State Physics / Materials Science. After acquiring his Ph. D. Degree from IIT Kharagpur Dr. M. Roy shifted to IIT Kanpur and later on IIT Bombay for his Post Doc. work. After his Post. Doc. work he joined on the Post of Assistant Professor at M. L.

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Introduction

Bismuth vanadate Bi₄V₂O₁₁ is a member of the Aurivillius homologous series $(Bi_2O_2)^{2+}$ $(A_{n-1}B_nO_{3n+1})^{2-}$ with n=1. It consists of Bi₂O₃ layers interleaved with the perovskite like sheets of V_2O_5 with the perovskite slab containing oxygen vacancies, responsible for the high ionic conductivity of oxide [1, 2]. The most attractive features of this compound are that of its strong polar response and high ionic mobility which are generally incompatible in most ferroelectrics [1, **3-4**]. It finds a wide variety of applications in catalysts, gas sensors, solid state electrolytes as electrode materials for lithium rechargeable batteries, pyroelectric detectors, fuel cells and oxygen pumps [5-7]. Single crystals of $Bi_4V_2O_{11}$ have been grown by slow cooling the melts of the prereacted compounds [4]. Bi₄V₂O₁₁ 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 [8-13]. This compound was also prepared in thin film form by chemical vapor deposition (CVD) method [14]. $Bi_4V_2O_{11}$ compound has three structural modifications; these modifications are α , β and γ form. The α -Bi₄V₂O₁₁ is found in mainly two structural form such as monoclinic crystal structure with space group C2/m and orthorhombic crystal structure with space group $P22_12_1$ [15, 16]. The β form is having the orthorhombic

crystal structure in the centrosymmetric space group Amam. The crystal structure of high temperature γ form is tetragonal with space group I4/mmm [2]. The phase transition for $Bi_4V_2O_{11}$ occurs from α to β at 720 K, β to γ at 840 K, and γ to γ' at 1150 K while γ' to liquid is at 1160 K [17]. Ferroelectric properties were reported for the low temperature α phase in Bi₄V₂O₁₁ [18]. Electrical properties of ceramics strongly depend on its microstructure, for example; sample with larger grains have lower conductivity [19-21]. Dielectric studies on nano crystalline $Bi_4V_2O_{11}$ powders indicated that the ferroelectric to paraelectric phase transition is strongly frequency dependent [22]. The Curie- Weiss law is valid above the transition temperature. Conductivity of BIVOX and BIMEVOX has been reported [23-28]. From the literature it is observed that most of the work have been reported related to γ phase but no systematic work has been reported on the low temperature α phase and hence we want to study the electrical and thermal behavior of low temperature α phase. In view of this the present paper reports on the synthesis, electrical and thermal properties of pure and 1%, Cu-doped Bi₄V₂O₁₁ compound in vanadium site.

Experimental

Materials and sample preparation

The polycrystalline ceramic samples of $Bi_4V_{2-x}Cu_xO_{11}$ (x= 0.0 and 0.02) were prepared by the conventional solid state reaction method. The stoichiometric amount of Bi_2O_3 (99.99%, HIMEDIA, Mumbai), V_2O_5 (99.0%, HIMEDIA, Mumbai) and CuO (99.99%, CDH, New Delhi) were mixed 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/cm² in a hydraulic press. These pellets were sintered at 800 °C for 2 h and 1 h respectively.

Characterization techniques

X-ray diffraction

Structural characterization of Bi₄V_{2-x}Cu_xO₁₁ (x=0.0 and 0.02) compounds was carried out by X-ray diffraction using Rigaku X-ray diffractometer with CuK α radiation and nickel filter in a wide range of 2 θ from 10-90° with a scanning rate of 2° per minute. The instrument was calibrated using the pure silicon sample provided with the instrument.

Dielectric constant and loss measurement

The dielectric constant (ϵ ') and dielectric loss (ϵ '') of Bi₄V_{2-x}Cu_xO₁₁ (x=0.0 and 0.02) compounds were measured as a function of frequency (100 Hz-2 MHz) and temperature (RT to 673 K) using a HIOKI 3532-50 LCR HITESTER.

Conductivity measurement

The ac conductivity (σ_{ac}) was measured at 100 kHz, in the temperature range of 300 K-693 K using the relation $\sigma_{ac}=\omega\epsilon_{o}\epsilon^{"}$. The dc electrical conductivity measurement was

carried out using laboratory made set up from room temperature to 653 K in air atmosphere using high precession digital pico ammeter Model (DPM-111).

Thermal analysis

The Modulated Differential Scanning Calorimetry (MDSC) measurement was carried out with TA instruments Model 2910 modulated differential scanning calorimeter from RT to 600 °C in inert (N₂) atmosphere with a heating rate of 5°C/min with ± 0.75 °C modulation per 60 sec.



Fig. 1. RT X-ray diffraction patterns of $Bi_4V_{2-x}Cu_xO_{11}$ (x=0.0 and x=0.02).

Results and discussion

Fig. 1 shows the room temperature (RT) X-ray diffraction patterns of $Bi_4V_{2-x}Cu_xO_{11}(x=0.0 \text{ and } 0.02)$ 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 **[16, 29]**.

The variation of dielectric constant (ϵ ') of Bi₄V₂₋ _xCu_xO₁₁(x=0.0 and 0.02) as a function of frequency (**Fig. 2**) indicates that, at lower frequencies ϵ ' decreases very fastly due to the space charge contribution but at higher frequencies the decrease is slow and become almost frequency independent due to the ionic and electronic contribution for both the compounds.



Fig. 2. Dielectric constant versus frequency curves of $Bi_4V_{2\mbox{-}x}Cu_xO_{11}$ (x=0.0 and 0.02).

The variation of dissipation factor of $Bi_4V_{2-x}Cu_xO_{11}$ (x=0.0 and 0.02) as a function of frequency at room temperature is shown in **Fig. 3**.



Fig. 3. Dissipation factor versus frequency curves of $Bi_4V_{2-x}Cu_xO_{11}$ (x=0.0 and 0.02).

The dissipation factor (ε '') shows almost similar behavior as dielectric constant. The temperature variation of ε ' for Bi₄V_{2-x}Cu_xO₁₁ (x=0.0 and 0.02) at a frequency of 100 kHz is shown in **Fig. 4**.



Fig. 4. Dielectric constant versus temperature curves of $Bi_4V_{2\mbox{-}x}Cu_xO_{11}$ (x=0.0 and 0.02) at a frequency of 100 kHz.

From the figure it is observed that ε' for 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 Cu-doped compound with x=0.02 shows an anomaly around 633K and then decreases rapidly. Further the peak value of ε' for x=0.02 is low (7400) which may be due to the increase in the grain size with the addition of Cu on vanadium site [30]. Further, the ionic radii of V⁵⁺ ion (0.59 Å) is smaller than that of the ionic radii of Cu²⁺ ion (0.73 Å), and hence, the grain size increases with the substitution of Cu²⁺ ions on vanadium site. The temperature variation of ε'' for Bi₄V_{2-x}Cu_xO₁₁ (x=0.0 and 0.02) at a frequency of 100 kHz is shown in **Fig. 5**. From the fig, it is observed that dissipation factor

increases with the increase of temperature and there is no peak observed up to the measured temperature range. The ac conductivity (σ_{ac}) was measured at 100 kHz, in the temperature range of 300 K-693 K using the relation $\sigma_{ac}=\omega\epsilon_{o}\epsilon^{"}$.



Fig. 5. Dissipation factor versus temperature curves of $Bi_4V_{2\mbox{-}x}Cu_xO_{11}$ (x=0.0 and 0.02) at a frequency of 100 kHz.

Fig. 6 shows the variation of $\log \sigma_{ac}$ versus 1000/T curve. The calculated activation energies (Ea) were 0.45 eV (323-533 K) and 0.93 eV (543-683 K) for x=0.0 and 0.05 eV(303-403 K),0.37eV(413-603 K) and 2.16 eV (613-683 K) for x=0.02 compound.



Fig. 6. $log\sigma_{ac}versus$ 1000/T curves of $Bi_4V_{2:x}Cu_xO_{11}$ (x=0.0 and 0.02) at a frequency of 100kHz.

The temperature dependence of dc conductivity (σ_{dc}) for Bi₄V_{2-x}Cu_xO₁₁ is shown in **Fig. 7**. The conductivity is too small to be measured below the temperature of 533 K. The activation energies calculated from log σ vs 1000/T curve are 1.85 eV for pure compound and 1.69 eV for Cudoped compound.

Fig. 8 shows the heat capacity and heat flow curves of $Bi_4V_2O_{11}$ as a function of temperature. The heat capacity curve as well as heat flow curve clearly indicates two thermal anomalies i. e phase transition around the temperature 440 °C and 515 °C. 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 $\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$ phase changes.



Fig. 7. $\log \sigma_{dc}$ versus 1000/T curves of $Bi_4V_{2-x}Cu_xO_{11}$ (x=0.0 and 0.02).



Fig. 8. Heat flow and heat capacity versus temperature curves for ${\rm Bi}_4 {\rm V}_2 {\rm O}_{11}.$



Fig. 9. Heat flow and heat capacity versus temperature curves for $Bi_4V_{1.98}Cu_{0.02}O_{11}.$

Fig. 9 shows the MDSC curves of $Bi_4V_{2-x}Cu_xO_{11}$ where x=0.02. Here the heat capacity curve shows two exothermic peaks representing $\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$ phase transitions around 462 and 512 °C whereas the heat flow curve shows two endothermic peaks around same temperature. Here both $\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$ transition temperatures are shifting in both the heat capacity and heat flow curves.

If we compare the transition behavior of Cu- doped and pure $Bi_4V_2O_{11}$ compound then it is observed that $\alpha \rightarrow \beta$ transition shifted from 440 °C in the pure compound to 462 °C (higher side) in the Cu doped compound and $\beta \rightarrow \gamma$ transition shifted from 518 °C in the pure compound to 512 °C (lower side) in the Cu doped compound. The shifting of transition temperature may further be explained on the basis of difference in ionic radii of the host and foreign atoms as mention above. In addition an additional peak around 450°C is observed in both the curves which is unknown and needs further explanation.

Conclusion

From the above studies, it is concluded that the substitution of Cu-ions on V-site in $Bi_4V_{2-x}Cu_xO_{11}$, decreases the dielectric constant and increases the ac conductivity of the compound. The dc conductivity increases slightly for Cudoped compound. The thermal behavior of the pure and dopedcompounds 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 higher and lower sides with respect to the pure compound which depends upon the thermal characteristics of Cu present on the vanadium lattice sites.

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