

Synthesis, Structure and Microstructure of $\text{Bi}_{1.5}\text{CuV}_{1.5}\text{O}_7$

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Abstract: Copper doped bismuth vanadate with nominal composition $\text{Bi}_{1.5}\text{CuV}_{1.5}\text{O}_7$ was synthesized using classical solid state reaction method. X-ray analysis confirm the formation of monoclinic phase in the as-prepared compound. Different grain size after primary investigation reveals the influence of dopant ions on the domain structure and its microstructure. The phase compositions behaviour was found to be strongly correlated with the partial substitution of heterovalent cation dopant. Energy dispersive spectra confirm the occurrence of stoichiometric elements within the synthesized compounds.

Keywords: Bismuth pyrochlore ceramics, Structure. Energy dispersive spectra, Microstructure.

1. Introduction

The manufacturing of highly integrated electronic devices for future gadgets, used in telecommunication and mobile communication systems sustained the improvement of modified microwave pyrochlore dielectric ceramics based technology. This has also kept a momentum in synthesizing the novel high frequency dielectric materials for the development of multilayer components and devices operating at wideband microwave frequency range [1]-[2]. Bismuth-based pyrochlore ceramics are such dielectric materials which has low sintering temperature ($< 900^\circ\text{C}$) and exhibit significant dielectric characteristics such as high dielectric constant (ϵ_r) and low tangent loss ($\tan \delta$), controllable temperature coefficients of α_ϵ and compatibility with Ag electrodes which can significantly ease the assembly cost [3]-[4].

The pyrochlore structure, of general formula $\text{A}_2\text{B}_2\text{O}_7$, contains a large A cation divalent or trivalent that typically prefer a site having eight coordination number and a smaller tetravalent or pentavalent cation B that typically occurs in octahedral sites [5]-[7]. It has sizeable compositional and structural flexibility, including the opportunity to put together a broad choice of dopant ions. Hence a partial or complete ion replacement, such as Cu^{2+} , Mg^{2+} , Sr^{2+} , Ce^{4+} , Zr^{4+} and Ti^{4+} , is normally used to improve the dielectric properties, especially to enhance dielectric constant and adjust temperature coefficient of dielectric constant [8]-[9]. It is well known fact that the structural stability of pyrochlores is generally governed by the radius ratio of A and B cations. Furthermore, the role of dopants at specific cationic site plays a very important role in understanding the structure-property relationship in ceramic compounds.

Hence, we have made an attempt to synthesize a modified bismuth vanadate compound doped with heterovalent copper and in this paper we report its preliminary structure and microstructure.

2. Experimental

Modified pyrochlore compound $\text{Bi}_{1.5}\text{CuV}_{1.5}\text{O}_7$ (BCV) was prepared using conventional solid-state reaction. Bi_2O_3 , CuO and V_2O_5 (All 99.5% pure) were mixed in an agate mortar for 3 h. The mixture was calcined twice at 650°C for 2 h in air. The calcined powder was milled again for 4 h, sieved and compacted in circular pellets and sintered at 690°C for 4 h. The phase composition of each sample was investigated by powder x-ray diffraction (XRD, Philips make, X'pert Pro PANanalytical model) using Ni -filtered CuK_α ($\lambda = 1.5406\text{\AA}$) radiation between $2\theta=10^\circ$ - 80° , with a step size of 0.02° with a scan step time 0.5 having sampling rate of 5 s step^{-1} . The XRD pattern was analyzed by the Rietveld method using the UNITCELL program. A pseudo-Voigt function was used to generate the line-shape of the diffraction peaks. The scanning electron micrograph (SEM) image and energy dispersive spectra (EDS) pattern were also obtained for the microstructure and elemental analysis of the polished samples using scanning electron microscope (Carl Zeiss EVO18 EDS Oxford).

3. Results and Discussion

X-ray diffraction pattern of the $\text{Bi}_{1.5}\text{CuV}_{1.5}\text{O}_7$ revealed the single phase nature of the compound. The powder xrd pattern was indexed based on monoclinic crystal symmetry. In order to clarify the influence of copper ion magnesium substitution in the structure, the lattice parameter and crystal symmetry were determined by Rietveld analysis.

Table 1 summarizes the structural data of $\text{Bi}_{1.5}\text{CuV}_{1.5}\text{O}_7$ ceramics. The Cu^{2+} ion partially occupy both the cationic sites.

Thus, the pyrochlore phase, $(\text{Bi}_{1.5}\text{Cu}_{0.5})(\text{Cu}_{0.5}\text{V}_{1.5})\text{O}_7$ is formed by the combination of two inter-penetrating networks consisting of BO_6 octahedra and A_2O tetrahedral plane.

Table 1: Structural data of $\text{Bi}_{1.5}\text{CuV}_{1.5}\text{O}_7$ ceramics

Ceramic sample	Lattice parameters (Å)			β (°)	Cell volume (Å) ³
	a	b	c		
BCV	7.7781	5.5317	7.6173	100.55	322.20

The large difference of the ionic radius between A and B cations was suggested as the reason for the instability of pyrochlore [10]. Further, the tolerance factor calculations contain more structural information, which gives further insight into the details of the structural stability features in the monoclinic $\text{Bi}_{1.5}\text{CuV}_{1.5}\text{O}_7$.

It has been reported that Bi^{3+} content demonstrates a strong effect on the phase progression in the Bi-based pyrochlores, and the distorted phase is suggested to result from the long-range coupling of the $6s^2$ lone-pair electrons of Bi^{3+} on the A-site position, which can be affected by the nature of B-site cations [11]. K. Sudheendran *et al* [12] communicated that broad Raman modes appears due to disordering of Zn^{2+} and Nb^{5+} ions at the B-site of the pyrochlore monoclinic $\text{Bi}_2\text{Zn}_{2/3}\text{Nb}_{4/3}\text{O}_7$ bulk and thin film. This can be correlated with our monoclinic $\text{Bi}_{1.5}\text{CuV}_{1.5}\text{O}_7$ bulk compound leading to pyrochlore phase formation because of change in Cu-O and V-O binding energy at $2\theta = 28.39^\circ$.

The microstructure of the synthesized compound exhibiting elongated dispersed grains is depicted in Figure 1(a) and 2(a). The grain size decreases with Cu^{2+} substitution and showed a bi-modal distribution in the microstructure.

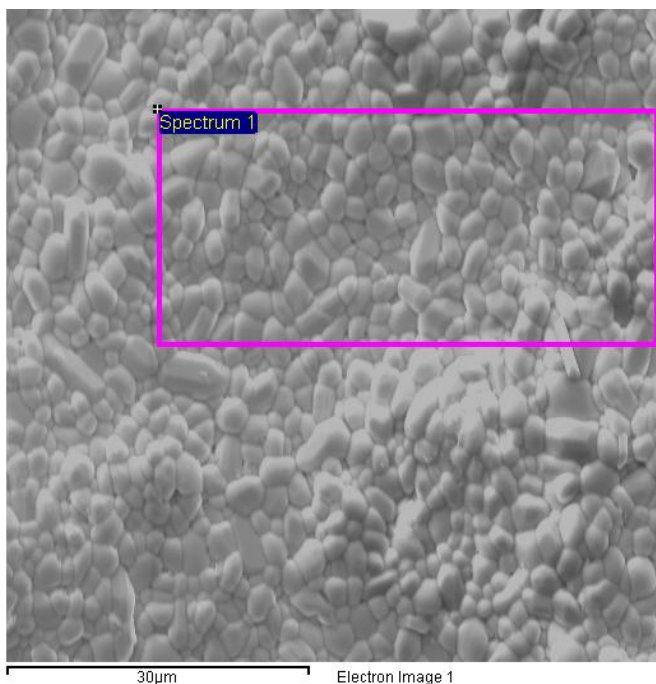


Figure 1(a): SEM of $\text{Bi}_{1.5}\text{CuV}_{1.5}\text{O}_7$ (Spectrum region 1)

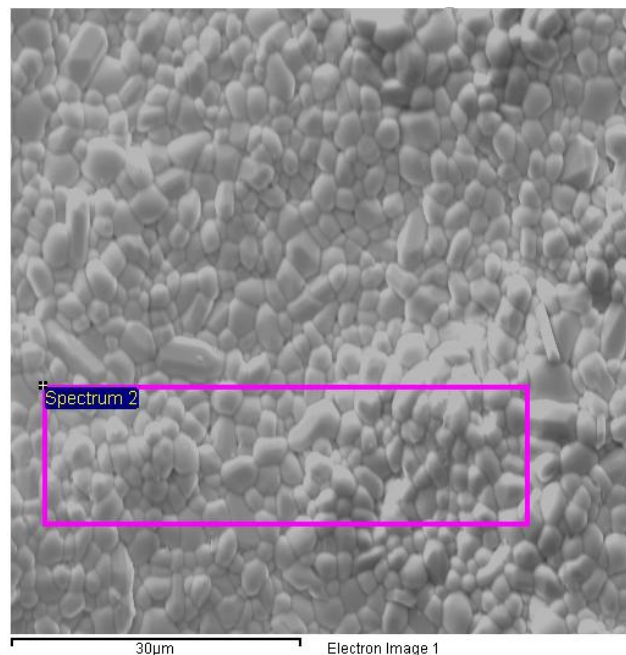


Figure 2(a): SEM of $\text{Bi}_{1.5}\text{CuV}_{1.5}\text{O}_7$ (Spectrum region 2)

As proposed by J C Nino *et al* [13], Cu^{2+} cannot establish a distorted coordination, which is required for the stabilization of the monoclinic structure. Energy dispersive spectral (EDS) pattern (Figure 1(b) and 2(b)) at two different region was also obtained for elemental analysis and individual element in wt% at two different regions is specified in Table 2. This confirms the occurrence of stoichiometric elements within the synthesized compound.

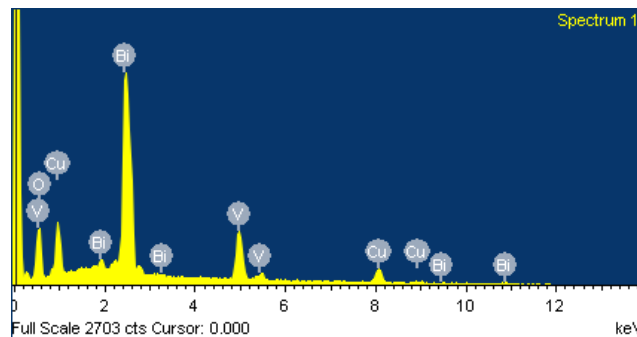


Figure 1(b): EDS of $\text{Bi}_{1.5}\text{CuV}_{1.5}\text{O}_7$ (Spectrum region 1)

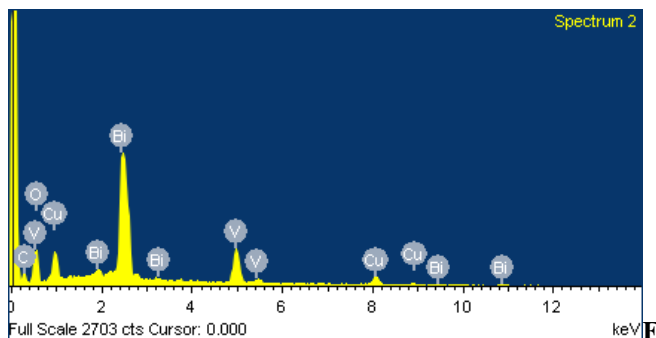


Figure 2(b): EDS of Bi_{1.5}CuV_{1.5}O₇ (Spectrum region 2)

Table 2: EDS data of Bi_{1.5}CuV_{1.5}O₇ ceramics

Spectrum Region	Wt%			
	O	V	Cu	Bi
1	14.28	13.29	14.31	58.12
2	15.60	13.85	12.54	58.00

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