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Structural and Dielectric Studies of CuO Doped $Sr_2Bi_4Ti_5O_{18}$ Ferroelectric Ceramics

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Abstract: CuO doped $Sr_2Bi_4Ti_5O_{18}$ ferroelectric ceramics were prepared by standard solid state reaction method. The prepared samples were investigated by XRD, Density, SEM, EDAX and Dielectric studies. Phase pure tetragonal structure was confirmed from XRD analysis. The highest density value of 6.70 g/cm^3 is obtained from density measurement. Microstructure and elemental analysis were done by SEM-EDAX studies. The Curie temperature of the prepared samples was found out by dielectric spectroscopic technique. The highest T_c of 313 ^oC is observed at the dopant level of 1.0 mol %. After adding CuO as dopant the dielectric properties were improved. This modified ferroelectric ceramics has potential applications in ferroelectric memory devices.
Keywords : Perovskite, Strontium Bismuth Titanate, Copper oxide, Curie temperature

1. Introduction :

Now a day's bismuth layered structure ferroelectric (BLSFs) materials got more attention due to their potential applications in the nonvolatile ferroelectric random access memory devices, resonators, actuators and for their lead free nature [1,2]. The lead based ferroelectric materials were highly toxic and avoided for practical applications [3]. To make the environment as lead free, the alternative ferroelectric materials were widely studied in last few decades [4-6]. BLSFs are belong to the family of Aurivillius oxides which having general formula as (Bi_2O_2)$^{2+}$ ($A_{m-1}B_mO_{3m+1}$)$^{2-}$. Where ($A_{m-1}B_mO_{3m+1}$)$^{2-}$ blocks are sandwiched between bismuth oxide (Bi_2O_2)$^{2+}$ layers along c axis, A is occupied by cation such as Na^+, K^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}, Bi^{3+} and La^{3+}, B is occupied by Tetra-, penta- and hexavalent ions and m denotes the number of BO_6 octahedra present in the pseudo-perovskite block respectively [7]. $Sr_2Bi_4Ti_5O_{18}$ (SBT) is one of the 5 layered (m = 5) BLSF material [8]. Due to its lead free nature and high Curie temperature (285 ^oC) this compound is also used in piezoelectric applications such as piezoelectric filters and high temperature sensors [9]. Several literatures were reported for CuO doped ferroelectric ceramics, which showing excellent improvement in their electrical properties after adding CuO [10-15]. In the present work CuO doped $Sr_2Bi_4Ti_5O_{18}$ ceramics with various doping concentration were synthesized and characterized. Structure, microstructure, elemental and dielectric studies were carried out in order to study the material performance after CuO doping.

2. Experimental :

2.1. Synthesis :

The $Sr_2Bi_4Ti_5O_{18}$ + x mol % CuO, where x = 0.0, 0.25, 0.50, 0.75 and 1.0 mol % ceramics were prepared by solid state reaction method using analytical grade carbonate powder and metal oxides purchased from Sigma-Aldrich, $SrCO_3$ (99.9 %), Bi_2O_3 (99.9 %), TiO_2 (99.9 %) and CuO (99.999 %). The powders were weighed in the stoichiometric ratio of the compositions and mixed thoroughly using agate mortar and pestle and calcined at 900 °C for 2h in air atmosphere. After calcination the mixture was again grounded and mixed thoroughly with PVA solution as binder and then the powders were pressed into 13 mm dia pellets by applying an pressure of 200 MPa. The pellets were covered by the calcined powder to minimize the evaporation of bismuth oxide and the binder is burned out by keeping the pellets at 300 °C for 1 hr, finally the samples were sintered at 1180 °C for 2h in air.

2.2. Characterization Techniques :

The sintered pellets were crushed into powder and XRD is taken with Cu Kα radiation (Bruker D8 Advance) to found out their crystalline structures. The microstructures and Element composition of the ceramics were observed using scanning electron microscope which was attached with EDAX (Hitachi, Model : S-3400N). The bulk density (ρ) of the ceramic pellets were measured by Archimedes' principle. Conducting silver paste is coated on the top and bottom surfaces of the samples for dielectric studies. The dielectric constant (ε_r) as a function of temperature at the frequency of 1 MHz were measured by using impedance analyzer (N4L - PSM 1735).

3. Results and Discussion :

3.1. Powder X-ray Diffraction Analysis :

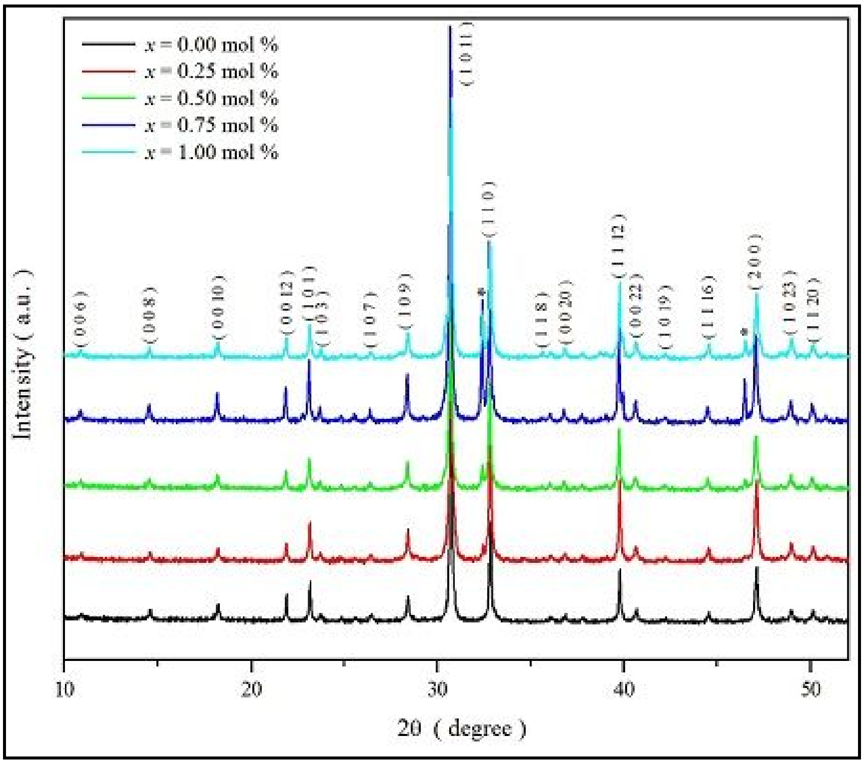

Figure 1. XRD patterns of SBT-CuO-*x* lead free ferroelectric ceramics.

Figure 1 shows the powder XRD patterns for CuO doped $Sr_2Bi_4Ti_5O_{18}$ ferroelectric ceramics. For undoped SBT ceramics, pure single phase bismuth layered structure was observed and indexed for orthorhombic symmetry in space group B2ab by using standard data (ICDD file no. 14 - 0276). It was found that after increasing the doping concentration the trace of secondary phase $SrTiO_3$ was observed (denoted as * in fig. 1). The similar observation was reported in literature for Ca doped SBT ferroelectric ceramics [16]. At the same time no CuO diffraction peaks were observed which means CuO doping creates new phase or it splits $Sr_2Bi_4Ti_5O_{18}$ into $SrBi_4Ti_4O_{15}$ and $SrTiO_3$ perovskite phases.

3.2. Density Measurement :

Figure 2 shows the experimental density values of the ceramic pellets as a function of CuO doping concentration. The optimum sintering temperature of the measured pellets are 1180 °C. The measured density values decreased by increasing the CuO content. For undoped sample the experimental density value is 5.74 g/cm^3. The maximum density value of 6.70 g/cm^3 is obtained for the doping content of 0.25 mol % and then the density value drops gradually. The measured experimental density values for all the CuO doped SBT pellets were given in table 1.

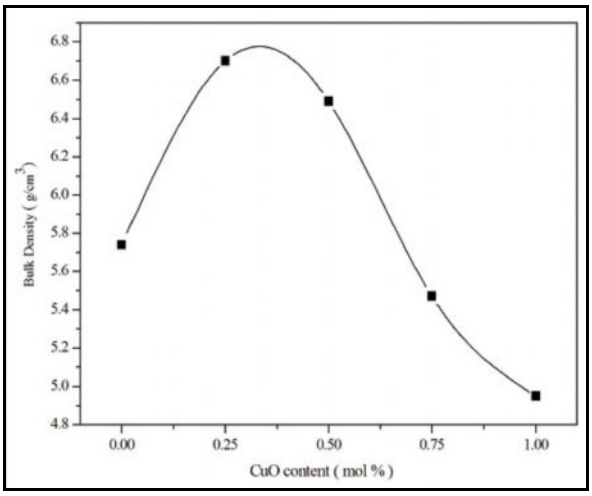

Figure 2. Bulk density values of the SBT-CuO-*x* ferroelectric ceramics.

3.3. Morphology and Composition Analysis :

Figure 3 shows the SEM images of the CuO doped SBT ferroelectric ceramics. In order to check the microstructure and grain size of the conventionally prepared samples, the pellets were subjected into SEM analysis. The SEM images clearly show the layered like growth mechanism of the SBT ceramics ie., BLSF's. The average grain size observed for the samples were around 1– 5 µm. After increasing the CuO content the grain size will increases simultaneously and it was clearly evidenced from SEM images. The grain sizes were increased well due to the large amount of CuO doping content (0.75 and 1.0 mol %).

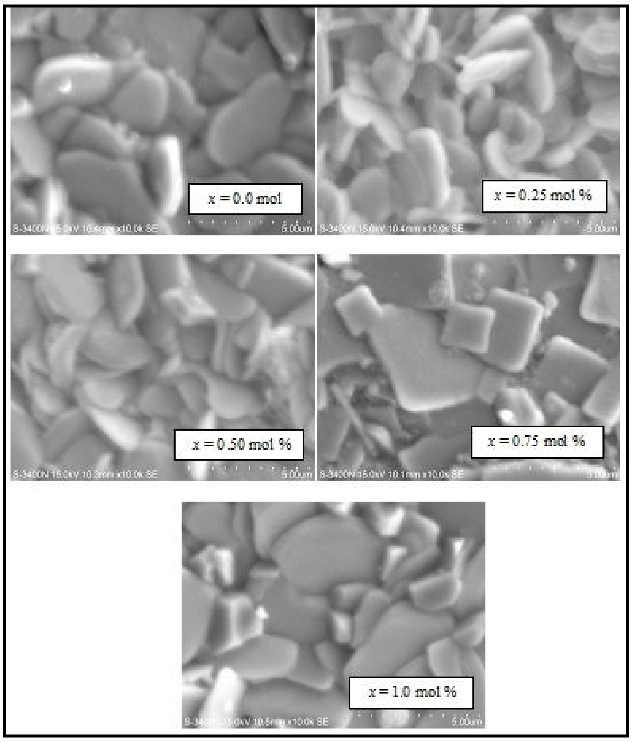

Figure 3. SEM images of the SBT-CuO-*x* ferroelectric ceramics.

Figure 4 shows the EDAX pattern for the corresponding CuO doped strontium bismuth titanate ferroelectric ceramics. To understand the actual composition of the prepared ceramics, the well sintered ceramic pellets were subjected to energy dispersive X-ray analysis (EDAX). It is clear from EDAX pattern that Sr, Bi, Ti, Cu and O elements were presented in the pellets according to their stoichiometric ratio. Figure 4 shows the weight percentage and atom percentage of the elements present in the material and also which are in good agreement with each other. Fig. 4 (a), (b), (c), (d) and (e) is the corresponding doping concentration of x = 0.0, 0.25, 0.50, 0.75 and 1.0 mol %.

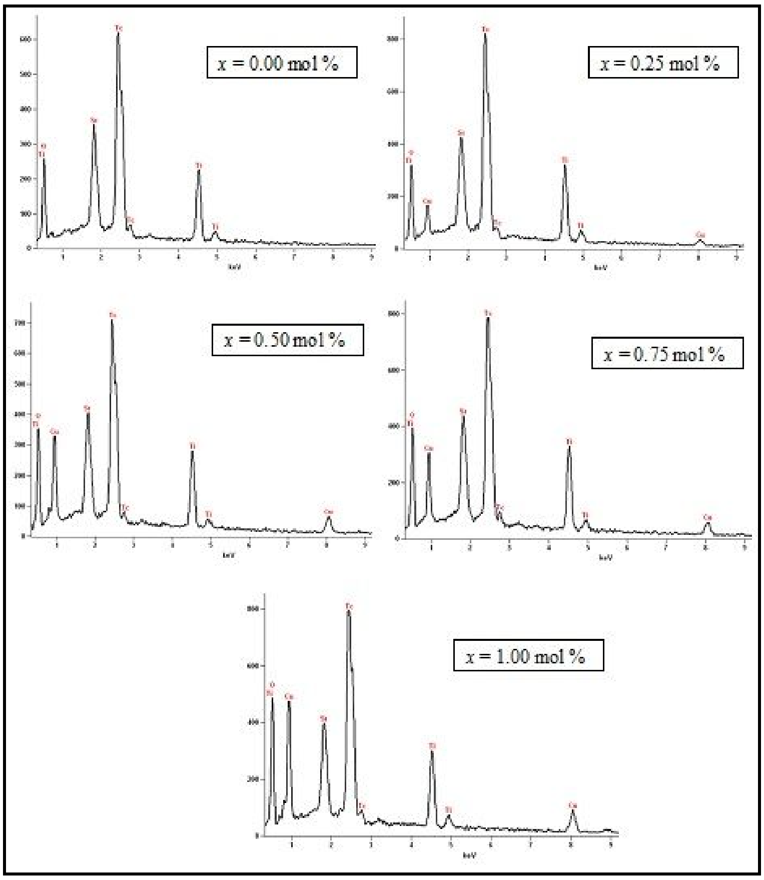

Figure 4. EDAX pattern for the SBT-CuO-*x* ferroelectric ceramics.

Figure 5 shows the temperature dependent dielectric constant of SBT-CuO-x (x = 0.0, 0.25, 0.50, 0.75 and 1.0 mol %.) ceramics at 1 MHz. The dielectric peaks show the sharp transition near its Curie temperature which indicates the normal ferroelectrics transition. It is observed that the T_c values simultaneously increases after introducing CuO to the SBT ceramics, which is clearly given in table 1. CuO content affect the cell volume of SBT ceramics, results in increasing the cell volume, structure distortion and oxygen vacancies are the possible reasons for enhancement in Curie temperature [17].

Table 1. Density and Curie temperature values of SBT-CuO-*x* ferroelectric ceramics.

CuO content in mol % (x)	Density (g/cm^3)	Curie temperature (^oC)
0.0	5.74	302
0.25	6.70	304
0.50	6.49	305
0.75	5.47	312
1.0	4.95	313

(a)

Element	Weight %	Atom %
O	46.07	81.20
Ti	9.92	5.84
Sr	11.34	3.65
Bi	32.67	9.31
Total	100.00	100.00

(b)

Element	Weight %	Atom %
O	45.03	80.24
Ti	10.24	6.09
Cu	2.36	1.06
Sr	10.64	3.46
Bi	31.73	9.15
Total	100.00	100.00

(c)

Element	Weight %	Atom %
O	47.35	81.44
Ti	10.05	5.77
Cu	3.70	1.60
Sr	10.13	3.18
Bi	28.77	8.01
Total	100.00	100.00

(d)

Element	Weight %	Atom %
O	47.83	81.81
Ti	9.12	5.21
Cu	4.50	1.94
Sr	10.65	3.33
Bi	27.90	7.71
Total	100.00	100.00

(e)

Element	Weight %	Atom %
O	45.85	80.38
Ti	9.45	5.54
Cu	6.77	2.99
Sr	9.54	3.05
Bi	28.39	8.04
Total	100.00	100.00

Figure 5. The elemental compositions of the SBT-CuO-*x* ferroelectric ceramics

3.4. Dielectric Studies :

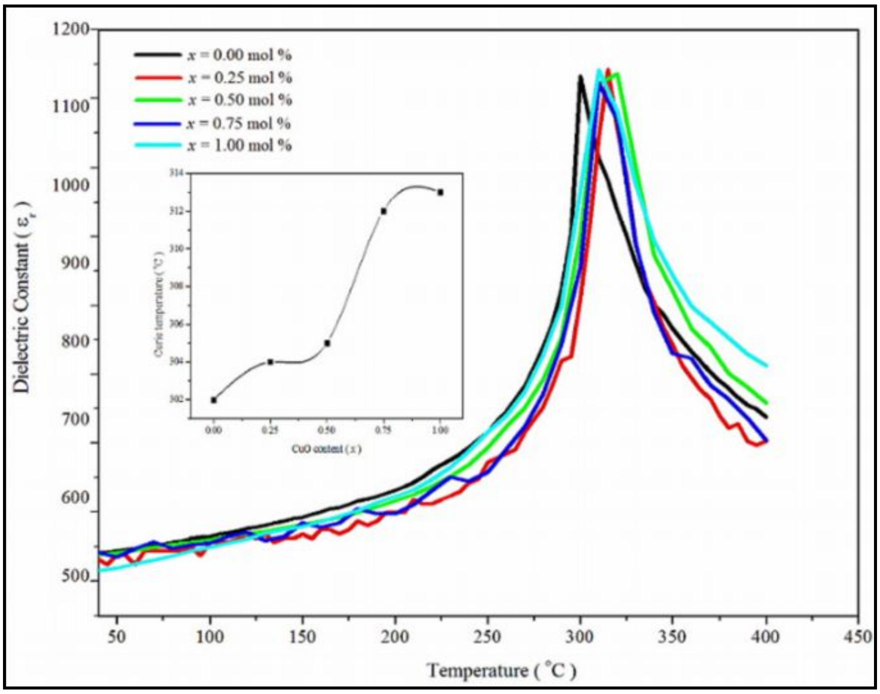

Figure 5. Temperature dependent dielectric plot of SBT-CuO-*x* ferroelectric ceramics.

4. Conclusion :

$Sr_2Bi_4Ti_5O_{18}$ + *x* mol % (where *x* = 0.0, 0.25, 0.50, 0.75 & 1.0 mol %) CuO doped lead free ferroelectric ceramics were prepared by conventional solid state reaction method.The effect of CuO addition on the structure, microstructure and dielectric properties were studied. After introducing CuO to the strontium bismuth titanate ceramics, the secondary phase of $SrTiO_3$ was formed and their Curie temperature was significantly enhanced. This material is a promising candidate for ferroelectric random access memory device fabrication.

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