Effect of CuO modification on dielectric, ferroelectric and piezoelectric properties of lead-free SrBi₄Ti₄O₁₅ ceramics

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Abstract
We report a systematic investigation of the structure, micro-structure, dielectric, ferroelectric and piezoelectric properties of CuO added SrBi₄Ti₄O₁₅ ceramics. All the samples were prepared by solid state reaction technique, where the wt% of CuO in SrBi₄Ti₄O₁₅ was varied as x = 0, 0.05, 0.2, 0.5. The addition of CuO increased the density of SrBi₄Ti₄O₁₅ ceramics which in turn resulted in the improvement of dielectric, ferroelectric as well as piezoelectric properties. However, no change either in the crystal structure or lattice parameter was observed with CuO addition. Further a dense micro-structure with improved electrical properties is expected to be due to liquid phase sintering. Raman spectra and specific heat measurements were also performed for getting further insight into the properties.

1. Introduction

Development of lead-free dielectric, ferroelectric or piezoelectric ceramics have been a challenging research problem in recent years. Bismuth layer structured ferroelectrics (BLSF) is a class of material which have been investigated extensively for the lead-free dielectric material [1]. Among the BLSF, the aurivillius family of compounds with the general formula (Bi₃O₂)₂⁺(Aₘ₋ₓBₘO₃m+1)²⁻ are having great importance because of its good dielectric, ferroelectric and piezoelectric properties. In the general formula, A-site can be occupied with Na⁺, K⁺, Ba²⁺, Ca²⁺, Sr²⁺, Bi⁴⁺, Ln³⁺, etc (monovalent, divalent or trivalent metal ion). The B-site can be occupied with Fe³⁺, Cr³⁺, Ti⁴⁺, Nb⁵⁺, W⁶⁺ (tetravalent, pentavalent or hexavalent metal ion) [2]. The m value indicates the number of perovskite layers interleaved with (Bi₂O₃)₂⁻ layer. SrBi₄Ti₄O₁₅ (SBTi) is a BLSF, which belongs to the above-mentioned group with m value equal to 4.

SBTi shows excellent properties such as high dielectric constant at room temperature (~200), high phase transition temperature (~520 °C), fatigue-free ferroelectric behavior and high dielectric breakdown strength [3]. It is a potential candidate for high temperature piezoelectric sensor and Ferroelectric RAM applications. However, the properties are not sufficient for replacing lead-based ceramics in the industry. For improving the properties of SBTi, researchers have been studied the effect of doping in various site of SBTi with different metal ions. Reports are available with lanthanum [4], praseodymium [5], erbium [6] barium [2] calcium [7], zirconium [8] niobium [9–11], vanadium [12], cobalt [13], tungsten [14], and molybdenum [10] doped SBTi systems.

Considering solid-state synthesis method for SrBi₄Ti₄O₁₅, due to the low melting point of Bi₂O₃ (~850 °C) the high temperature (~1100 °C) sintering process results the volatilization of Bi₂O₃ from SBTi. The volatilization of Bi₂O₃ leads to the formation of bismuth ion as well as oxygen ion vacancies in SBTi, this is the common and major defect associated with SBTi [3]. These defects leads to the poor density as well as the poor electrical properties in SBTi. So, for reducing the volatilization of Bi₂O₃ it is important to control the sintering process. For decreasing the sintering temperature and controlling the sintering process the importance of use of small amount sintering aid is reported by many researchers [15, 16]. Hence, in the current article we investigated
the effect of CuO modification on the dielectric, ferroelectric and piezoelectric properties of SBTi. The CuO is a well-known sintering aid, which can influence the density as well as electric properties of SBTi [17, 18].

2. Experimental

2.1. Synthesis

The’x’wt% (x = 0, 0.05, 0.2, 0.5) CuO modified SrBi₄Ti₄O¹₅ (SBTi-xCuO) ceramic have been synthesized by solid-state reaction method. The analytical grade metal oxide and carbonates such as SrCO₃ (Sigma-Aldrich, 99.9%), Bi₂O₃ (Sigma-Aldrich, 99.9%), TiO₂ (Sigma-Aldrich, 99.9%) and CuO (Sigma-Aldrich, 99.9%) were used as the starting precursors. For the synthesis of SrBi₄Ti₄O¹₅ powder the stoichiometric ratios of SrCO₃, Bi₂O₃, and TiO₂ were taken, and an extra 5wt% of Bi₂O₃ was added to the stoichiometric amount to compensate for the volatility of bismuth at high temperature. The oxide powders were mixed thoroughly in a planetary ball mill (FRITSCH) using Zirconium jars and balls. The milling was performed for 24 h at 150 rpm in acetone medium. The mixture obtained after ball milling was dried for 3 h in a hot air oven. The dried powders were calcinated using a covered alumina crucible at 1000 °C for 3 h with a heating and cooling rate of 5 °C min⁻¹. Different wt% (x = 0, 0.05, 0.2, 0.5) of CuO was added to the calcinated SrBi₄Ti₄O¹₅ power and ground thoroughly with agate mortar and pestle. The pure and CuO modified powders were pelletized into 10 mm diameter dies by applying 4 Tons pressure using a uni-axial press. The pellets were sintered at 1100 °C for 2 h with a heating and cooling rate of 5 °C min⁻¹. The pellets were used for recording the XRD spectrum, specific heat measurement, SEM image, dielectric, ferroelectric and piezoelectric measurement. The powder sample obtained by breaking the sintered pellets were used for taking the Raman spectrum.

2.2. Characterization

The room temperature XRD pattern (PANalytical-Empyrean, Netherlands, CuKα radiation) were recorded in the diffraction angle (2θ) range from 10° to 90° with step size of 0.02°. The room temperature Raman Spectra (STR 500 Confocal Micro Raman Spectrometer, India) were taken using an excitation wavelength of 532 nm with the power of 3.5 mW in the frequency range of 100 to 1000 cm⁻¹. The differential scanning calorimetry (DSC 404 F1 Pegasus from Netzsch) measurement were taken from 30 °C to 600 °C in a nitrogen atmosphere with a flow rate of 20 ml min⁻¹. The surface morphology of the sintered samples were examined using the scanning electron microscopy (CAREL ZEISS,EVO-18). Conductive silver paste was applied on the parallel surface of the pellet for making electrodes for dielectric, ferroelectric and piezoelectric measurements. Ferroelectric measurements were carried out at room temperature at a frequency of 50 Hz using PE loop tracer (Marine India). The temperature- dependent dielectric permittivity (Wayne Kerr Impedance Analyzer 6500B) was measured in the temperature range from 100 °C to 650 °C at 1 MHz. The samples were poled by DC electric field of 10 kV cm⁻¹ for 30 min at 250 °C, before the piezoelectric constant (d₃₃) measurement (YE2730A piezometer).

3. Result and discussion

3.1. Phase composition and Microstructural analysis

All the peaks in the XRD pattern were matched with SBTi (JCPDF card number 43–0973). There were no additional peaks compare to any secondary phase observed in SBTi-xCuO samples. The SBTi peaks were indexed based on an orthorhombic cell associated with A 2ₑ am space group [3]. The XRD pattern was analyzed by rietveld refinement (shown in figure 1) using jana 2006 software and the lattice parameters were calculated within the error limit ±0.002 Å [19]. The reliability factors, lattice parameters are given in table 1. From the XRD analysis, it can be concluded that the crystal structure is unaffected by the addition of CuO.

Figure 2 shows the SEM images of SBTi-xCuO ceramics. The plate-like structures have been identified from the SEM images of all samples. The average length of the grains (Grain Size) were calculated using ImageJ software and are given in table 1. The addition of CuO has decreased the grain size of SBTi. For CuO added samples, the edges of the grains are the irregular shape and thin compared to SBTi grain edges. It indicates the liquid-phase sintering effect of CuO. The action of CuO as a sintering aid in SBTi is clearly visible from the SEM images.

3.2. Raman spectrum

The Raman spectra recorded at room temperature are shown in figure 3(a). The exact peak frequency of different Raman active modes were obtained from the Gaussian fit of Raman data of SBTi (shown in figure 3(b)). The reported Raman active modes of SBTi and their possible reasons are listed in table 2. The observed Raman active modes were completely matched with reported Raman active modes of SBTi. From the figure 3(a), it is
clear that there are no additional modes present in the CuO added SBTi samples. The observation is consistent with the XRD spectrum that the crystal structure and the bond length are unaffected by CuO modification. However, a broadness in peak as well as the increase in intensity of the peak after the addition of CuO were observed. The increase in intensity can be correlated with the observed improvement in density.

### 3.3. Dielectric study

Figure 4 shows the dielectric constant as a function of the temperature of SBTi-xCuO samples. It can be clearly understood from the curve that the addition of CuO has improved the dielectric constant and decreased dielectric loss. The reason for the improved dielectric constant can be understood from the increased density (given in Table 3). The improvement in density is due to the sintering aid property of CuO. The presence of CuO at the time of sintering makes a liquid phase along the grain boundary, and it might prevent the evaporation rate.
of Bi$_2$O$_3$. The liquid phase sintering of grains are also clear from the SEM images (figure 2). The major defects in SBTi is the loss of Bi$_2$O$_3$ during sintering (due to low melting point of Bi$_2$O$_3$) and thereby the formation of Bi$^{3+}$ ion vacancies along with oxygen vacancies [3] (given in equation (1) using kronger-vink notation). The other defects are the occurrence of single or doubly ionized oxygen vacancies (for compensating lower oxygen partial pressure of sintering system) due to high temperature sintering (equation (2) and (3)) [21]. These vacancies

![SEM images of SBTi-xCuO ceramics.](image1)

![Room temperature Raman Spectra of SBTi-xCuO ceramics](image2)

![Gaussian fit of Raman spectra of SBTi.](image3)
increase the conductivity and the lossy nature of SBTi. So, the CuO sits along the grain boundary of SBTi might helps to reduce the formation of oxygen vacancies, thereby creating an increased density as well as improved electrical properties.

$$\text{Bi}_2\text{O}_3(\text{solid}) \rightarrow 2(\text{BiO})(\uparrow ) + \frac{1}{2}\text{O}_2(\uparrow ) + V_0 + 2\epsilon'$$

$$\text{O}_6^x \rightarrow \frac{1}{2}\text{O}_2(\uparrow ) + V_0^- + 2\epsilon'$$

$$V_0^- \equiv V_0 + \epsilon'$$

For further understanding the nature of phase transition, the dielectric data were analyzed with Curie-Weiss law equation (4) and modified Curie-Weiss law equation (5) given below [22],

$$\frac{1}{\epsilon_r} = \frac{T - T_0}{\Phi}$$

(4)

$$\frac{1}{\epsilon_r} - \frac{1}{\epsilon_m} = \left(\frac{T - T_0}{\Phi}\right)^\gamma$$

(5)
Where $\varepsilon'_r$ is the real part of relative permittivity or dielectric constant, $T_D$ is the Curie-Weiss temperature and $\Phi$ is the Curie constant. The plot between $\frac{1}{\varepsilon'_r}$ and temperature gives a straight line with a slope of $\frac{1}{\Phi}$ and the $x$-axis intercept at $T_D$. (shown in figure 5(a)). The $\Upsilon$ is the degree of diffuseness, $\Phi'$ is the Curie-like constant, $T_c$ is the phase transition temperature and $\varepsilon'_m$ is the maximum value of dielectric constant at phase transition temperature $T_c$. The slope of the $\ln\left(\frac{1}{\varepsilon'_r} - \frac{1}{\varepsilon'_m}\right)$ versus $\ln(T - T_c)$ plot will give the degree of diffuseness $\Upsilon$. (shown in figures 5(b), 6(a)). All the calculated parameters from curie-weiss law and the modified curie-weiss law are listed in table 3. The obtained value of degree of diffuseness $\Upsilon$ for all samples are close to one indicates the nature of phase transitions are normal phase transitions [23].

### 3.4. Specific heat capacity at constant pressure

Three subsequent runs of differential scanning calorimetry (DSC) were performed empty crucibles, crucibles containing standard Sapphire and crucible with sample for calculating the specific heat. The segments in the DSC measurement includes two isothermal segments in the beginning and the end. The specific heat was calculated from the ration method [24]. The specific heat measurements are done to ascertain the thermal stability as well as phase changing nature of samples. Figure 6(b) shows the variation of specific heat with temperature of SBTi-xCuO samples. It is clear from the figure that the addition of CuO has increased the value of specific heat capacity of SBTi. It shows that the thermal stability of the samples improved by the addition of CuO. From the figure 5(b) it is clear that at up to 300°C the specific heat capacities were increased with an increase in temperature, and above 300 °C it becomes nearly a constant. The high temperature (above 300 °C) behavior can
be understood from the Dulong-Petit law [25], which is approximated as,

\[ C_p = NRT \]  

where \( N \) is the number of ions, \( R \) is the gas constant, and \( T \) is the temperature. Comparing with pure SBTi, there is an increment in the value of \( C_p \) for CuO added SBTi. This increment indicates the increment in number of ions \( N \) in the CuO added samples. The increment in the number of ions \( N \) might be due to the reduced oxygen vacancies in the CuO added SBTi. The observed increase in density of CuO added SBTi also consistent with this argument. The phase transition was observed as a dip in the \( C_p \) curve (shown as ‘\( * \)’ in figure 6(b)) and the inset of figure 6(b) shows the zoomed portion of dip. The observed phase transition temperature from \( C_p \) measurement exactly matched with the observation from dielectric constant.

3.5. Ferroelectric and piezoelectric properties

Figure 7 shows the ferroelectric hysteresis loop of SBTi-xCuO composites. The observed parameters from ferroelectric and piezoelectric measurements are tabulated in the table 4. From the table one can conclude that the ferroelectric and piezoelectric properties are slightly improved by the addition of CuO into SBTi. The addition of CuO increased the maximum polarization and remanent polarization of SBTi. The coercive field is unaffected by the addition of CuO. The improvement in piezoelectric coefficient of CuO added SBTi can be understood from the increase in density as well as the decrease in dielectric loss.

4. Conclusions

The present work demonstrates the effect of \( x \) wt% \( (x = 0, 0.05, 0.2, 0.5) \) of CuO addition on electrical properties of lead-free bismuth layered oxide SrBi\( _4 \)Ti\( _4 \)O\( _{15} \), prepared by solid state reaction route. The addition of
CuO improved the density of SBTi. The dielectric, ferroelectric, as well as piezoelectric properties, of SBTi also shows an improvement by the addition of CuO. The XRD, Raman spectra confirm that there is no secondary phase formed due to the addition of CuO. The addition of CuO decreased the grain size of SBTi. The irregular and thin shaped grain boundaries of SBTi-CuO SEM images show the sintering aid effect of CuO. The phase transition temperature was unaffected by the addition of CuO. The specific heat at constant pressure indicates the improved thermal stability of CuO added SBTi. The maximum ferroelectric and piezoelectric properties were observed for SBTi-0.2CuO samples. The reason for improved properties have been explained using the sintering aid property of CuO. The observed increase in Dielectric, piezoelectric properties are comparable with the observed properties in niobium, cobalt doped SBTi.

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References

[1] Nayak P, Badapanda T, Pattanayak R, Mishra A, Anwar S, Sahoo P and Panigrahi S 2014 Metallurgical and Materials Transactions A 45 2132-41
[2] Nayak P, Badapanda T, Anwar S and Panigrahi S 2015 Phase Transitions 88 430–44
[3] Jose R et al 2018 RSC Adv. 8 34437–48
[4] Nayak P, Badapanda T and Panigrahi S 2017 J. Mater. Sci., Mater. Electron. 28 625–32
[5] Zou H, Hu Y, Zhu X, Sui Y, Wang X and Song Z 2015 Ferroelectrics 488 62–70
[6] Peng D, Zou H, Xu C, Wang X, Yao X, Lin J and Sun T 2012 AIP Adv. 2 042187
[7] Shan D, Qian X F, Wang W and Chen X B 2007 Integr. Ferroelectr. 94 64–72
[8] Nayak P, Badapanda T, Singh A K and Panigrahi S 2017 RSC Adv. 7 16319–31
[9] Hao H, Liu H and Ouyang S 2009 J. Electroceram. 22 357–62
[10] Jin C, Zhu J, Mao X Y, He J H, Shen I C and Chen X B 2006 Integrated Ferroelectrics 85 39–47
[11] Jin C, Du C p, Zhu J, He J h, Mao X Y and Chen X B 2006 J. Phys. D: Appl. Phys. 39 2415
[12] Zhu J, Mao X Y and Chen X B 2004 Solid State Commun. 130 363–6
[13] Wang Q, Cao Z P, Wang C M, Fu Q W, Yin D F and Tian H H 2016 J. Alloys Compd. 674 37–43
[14] Nayak P, Badapanda T and Panigrahi S 2016 J. Mater. Sci., Mater. Electron. 27 1217–26
[15] Moghadam H A and Barzegar A 2017 Journal of Materials Science: Materials in Electronics 28 13161–7
[16] Li J 2013 Bull. Mater. Sci. 36 877–81
[17] Elsayasperumal E and Malathi M 2016 Ceram. Int. 42 5830–41
[18] Kwok K and Wong H 2009 J. Phys. D: Appl. Phys. 42 095419
[19] Peňiček V, Dušek M and Palatinus L 2014 Zeitschrift für Kristallographie-Crystalline Materials 229 345–52
[20] Hao H, Liu H, Cao M, Min X and Ouyang S 2006 Appl. Phys. A 85 69–73
[21] Chen Y, Xie S, Wang H, Chen Q, Wang Q, Zhu J and Guan Z 2017 J. Alloys Compd. 696 746–53
[22] Jeyakanthan M, Subramanian U, Tangsali R, Jose R and Saravanan K V 2019 J. Mater. Sci., Mater. Electron. 30 14657–68
[23] Coondoo I et al 2018 J. Electron. Mater. 47 5870–8
[24] Standard A 2011 ASTM A annual Book of Standards 14
[25] Puri R and Babbar V 1998 Solid State Physics and Electronics

Table 4. Measured parameters from piezoelectric, ferroelectric hysteresis loop.

| Sample name | P_{max}(\mu C \text{ cm}^{-2}) | P_{r}(\mu C \text{ cm}^{-2}) | d_{33}(\mu C / N) |
|-------------|-----------------|-----------------|-----------------|
| SBTi        | 1.8             | 1               | 9               |
| SBTi-0.05CuO| 2.2             | 1.3             | 10              |
| SBTi-0.2CuO | 3.3             | 2               | 13              |
| SBTi-0.5CuO | 3               | 1.6             | 12              |