Dielectric Characterization and AC Impedance Studies of Composite Ceramics $x$BiFeO$_3$-(1-$x$)Sr$_2$Bi$_4$Ti$_5$O$_{18}$

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Abstract. The $x$BiFeO$_3$-(1-$x$)Sr$_2$Bi$_4$Ti$_5$O$_{18}$ (SBFTi-$x$, $x=0$, 0.1, 0.3 and 0.5) composite ferroelectric ceramics were prepared by sol-gel with self-propagating combustion method. The dielectric properties and AC impedance were analyzed. Six-layered Aurivillius structure was confirmed from the X-ray analysis. With the increasing of BiFeO$_3$ content, Bi$^{3+}$ and Fe$^{3+}$ co-doped in A and B site cause the lattice distortion in SBFTi-$x$ ceramic, and the Curie temperature continuous increasing and the dielectric peak gradually broadened due to disordered distribution of ions. Besides, The electrical structure in SBFTi-$x$ ceramics become uniform and all samples show negative temperature coefficient characteristics. Space charge polarization and mixed relaxation processes were also found in SBFTi-$x$ ceramics.

Introduction

Materials with the generic formula $(\text{Bi}_2\text{O}_2)^{2+} (\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$ (where A= Bi, B= Ti, Fe and $m$ denotes the number of BO$_6$ octahedra) belong to a large family of layered structure compounds. These are commonly referred to as bismuth layer structured ferroelectrics (BLSFs) and there is a growing interest in such compound in view of possible applications for nonvolatile memory devices[1-4]. However, the small remanent polarization values and poor fatigue behavior limit its practical application. And the use of elemental doping, combined with other ferroelectric or ferrous materials becomes the main way to improve the ferroelectric properties of BLSFs[5-7]. It is effective to improve the performance of BLSFs by forming solid solutions with two kinds of different bismuth layered structure or perovskite structure material which can be complementary to each other[8-10]. Similar compounds in the solid solution system of Bi$_4$Ti$_3$O$_{12}$+nBiFeO$_3$ (where $n=1$) have exhibit excellent ferroelectric properties and coupling phenomena as ferroelectromagnetism[11-14]. The $(\text{Bi}_2\text{O}_2)^{2+}$ layers in BLSFs play the key role as both space-charge compensation and insulation, with an expectation able to further reduce the leakage[12].

Recently, compounds from the SrBi$_4$Ti$_3$O$_{15}$ (SBTO$_{15}$, $m=4$) with BiFeO$_3$ (BFO) have been studied and it was found that SrBi$_3$FeTi$_4$O$_{18}$ (SBFTi, $m=5$) also belongs to the BLSF family of compounds which can show ferroelectric and antiferromagnetic nature giving rise to the “magnetolectric effect” (ME)[15] under the action of external magnetic fields. There are many reports about synthesis and electrical characterization of five-layered Aurivillius SrBi$_3$FeTi$_4$O$_{18}$ ceramics[16-18]. Motivated by these results and looking for a material where ferroelectric and magnetic orders coexist, we choose Sr$_2$Bi$_2$Ti$_5$O$_{18}$ with five-layer structure, compounded it with BiFeO$_3$. And we report here the dielectric properties and AC impedance of Aurivillius $x$BiFeO$_3$-(1-$x$)Sr$_2$Bi$_4$Ti$_5$O$_{18}$ composite ceramics for four compositions ($x=0$, 0.1, 0.3 and 0.5). To our knowledge, there are few reports about these compounds.
Experiment

$xBiFeO_3-(1-x)Sr_2Bi_4Ti_5O_{18}(SBFTi-x, x=0, 0.1, 0.3$ and $0.5)$ composite ceramics were prepared by sol-gel with self-propagating combustion method. The $Sr_2Bi_4Ti_5O_{18}$(SBTi) and BiFeO$_3$(BFO) precursor solutions were prepared by dissolving strontium acetate, bismuth nitrate, tetrabutyl titanate and ferric nitrate in ethylene glycol at room temperature. Acetylacetone was added to stabilize the solution. 10mol% excessive bismuth was used to compensate the evaporation of bismuth during the sintering process. The precursor solutions of SBFTi-$x$ were dried in a drying oven at 60°C~80°C for 10h and finally the fluffy precursor powders were obtained. The obtained powders were calcined at 500°C for 2h to remove a large amount of organic matter. The pre-calcined powders were thoroughly mixed with ethanol in a ball mill for 15 h, and then pressed into pellets with diameter of 10mm, the thickness of about 1mm disc (pressure 160MPa). Then the pellets were sintered in air at 1060°C~1120°C for 8h and followed by furnace cooling.

The crystal structures of the ceramics were determined by X-ray diffraction (XRD) method using D8-ADVANCE X-ray diffraction with Cu Ka radiation ($k = 0.54184$ nm) at a tube voltage of 40 kV and a tube current of 40 mA. The pellets were filed and polished to a thickness of about 0.5 mm and then electroded with silver for dielectric property measurements. Dielectric properties, ac conductivities were measured with a precision impedance analyzer (E4980A, Agilent, Santa Clara, CA) (20 Hz~2 MHz).

Results and Discussion

XRD Analysis

Figure 1(a) show the X-ray diffraction patterns (XRD) of the SBFTi-$x$ ($x=0, 0.1, 0.3$, and $0.5$) composite ceramics. These compounds are found to consist of a pure bismuth layer perovskite structure and their patterns can be matched well with the six-layered Aurivillius structure $Bi_7Fe_3Ti_3O_{21}$(Space group Fmm2, JCPDS:54-1044). However, with $x$ increasing, the second phase which was reported as cubic structure appears [19]. This is consistent with the results found by Wang [20] et al. in strontium doped $Bi_7Fe_{1.5}Co_{1.5}Ti_3O_{21}$. The $(1131)$ plane diffraction peaks shift to the lower angles with the substitution of $Fe^{3+}$ for $Ti^{4+}$ and $Bi^{3+}$ for $Sr^{2+}$ and then to the higher angles from Fig.1(b), which due to the incorporation of ionic radii[21-23]. The deviation of the diffraction peak angle indicates lattice distortion and it is the largest in SBFTi-0.3 ceramic.

![Figure 1. XRD pattern of the SBTi and SBFTi-x(x=0.1, 0.3 and 0.5) ceramics sintered at 1060°C (a) 20°~60°; (b) 29.5°~31.5°.](image-url)
Dielectric Analyses

The temperature dependence of the dielectric permittivity ($\varepsilon'_r$) and dielectric loss (tan$\delta$) of SBTi and SBFTi-x ceramics at different frequencies (1 KHz, 10 KHz, 100 KHz, and 1 MHz) is shown in figs.2, respectively. As can be seen, $\varepsilon'_r$ values show a frequency independent maxima in the range 280-400°C depending on the BFO content in the samples, corresponding to the Curie temperature ($T_c$) of paraelectric-ferroelectric phase transition. Below the transition temperature, the frequency dispersions of $\varepsilon'_r$ are very small. However, the dispersions become prominent above $T_c$. The increase in the value of $\varepsilon'_r$ at low frequency and high temperature can be interpreted in terms of polarization of mobile charge carries, presumably oxygen vacancies activated at high temperatures[17,24-25]. The dielectric peaks of SBFTi-x (x=0.3 and 0.5) ceramics are found to be broadened when compared to SBTi ceramic and this anomaly is attributed to the random arrangement of cations in the structure, leading to the microscopic heterogeneity in the composition due to the presence of different cations occupying A and B sites randomly in the crystal[17]. Besides, the presence of different relative proportions of Fe$^{3+}$ and Fe$^{2+}$ may be an additional contribution to the cation disorder [7].

Figure 2. Temperature dependence of dielectric constant $\varepsilon'_r$ and loss tan$\delta$ at different frequency of SBTi and SBFTi-x (x=0.1, 0.3 and 0.5) ceramics.
AC Impedance Analyses

The electric contributions of the microstructural inhomogenities can be separated by assigning the values of resistance (R) and capacitance (C) to each of them. In a complex impedance plane, grain, grain boundary, grain–electrode effects appear as a semicircles, whose centers lie on a line below the real axis[17]. Fig. 3 shows the Nyquist (Cole–Cole) plot with imaginary part of impedance (-Z") as a function of the real resistive part (Z'), at different temperatures. Each point in the plot corresponds to different frequency in the measuring frequency range. Semicircles are observed only after 280°C. The depression of semicircles is a result of the distribution of relaxation times unlike the pure Debye relaxation case[17,26]. The high frequency semicircle represents the bulk (grain) property of the material arising due to the parallel combination of bulk resistance (R_b) and bulk capacitance (C_b) of the material. Another semicircular arc in the low frequency region is due to grain boundary (gb) effect, which is equivalent to the parallel combination of the R_gb and C_gb.

As can be seen from Fig.3, the plots in the complex plane above 280°C of SBTi and SBFTi-0.1 ceramics consist of two semicircles with their centers lying below the real axis. However, it is not
much clear in SBFTi-0.3 and SBFTi-0.5 ceramics. The assignment of these two semicircular arcs to the electrical response due to grain interior and grain boundary is consistent with the “brick-layer model” [27] for a poly crystalline material. This shows the macro resistance of SBTi ceramic is mainly from the grain and grain boundary. As increasing of BFO, there are not much differences between the grain and grain boundary for the contribution of macro resistances in SBFTi-x (x=0.3 and 0.5) ceramics. With the increase of the test temperatures, the macroscopic resistances of all the ceramics decrease gradually, which is due to the easier diffusion and migration of the carriers. And it is probably the main reason that the largest lattice distortion in SBFTi-0.3 ceramic for its maximum macro resistance.

![Figure 4](image-url)

**Figure 4.** Frequency dependence of $-Z''$ and $M''$ for SBTi and SBFTi-x(x=0.1, 0.3 and 0.5) ceramics at different temperatures.

**Conclusions**

In order to study the relaxation process more deeply, Fig. 4 depict the variation of $Z''$ and $M''$as a function of frequency at different temperatures from 200°C to 480°C. From $Z''$-F an asymmetric peak appears at a particular frequency, known as Debye-like peak, which usually indicates the presence of space charge polarization process[16-17,28]. The values of $Z''_{\text{max}}$ decrease with increasing temperature and gradually move toward the high frequency, indicating that there is a mixed relaxation in SBFTi-x ceramics. With the increasing of frequency, $Z''$ is gradually widened at different temperatures, which means that the diffusion process of relaxation time occurs in the material, and there is a certain deviation from the ideal Debye relaxation [16-17, 28]. At low temperatures, the conductivity is low and the impedance is high. The values of $Z''$ fall monotonously at same frequency with increasing of temperature and $Z''$ show minor variations near
the plateau of frequencies. The above phenomenon is observed only when it is up to 200℃, therefore, SBFTi-x ceramic internal conductance behavior may be due to relaxation caused by defects, including electronic/oxygen ions/vacancies in the original position of the transition. Due to the presence of space charge polarization at lower frequencies, the $Z''_{\text{max}}$ value decreases gradually with the increase of frequency and temperature, and all the curves appear to merge at the higher frequency with disappearance of space charge polarization[16-17,28-29]. Besides, it is clear to see from Fig.4 that $M''_{\text{max}}$ does not coincide with $Z''_{\text{max}}$ at any given temperature and $M''$ peaks occur at higher frequencies than $Z''$ peaks. This indicates that there is a high concentration of Fe$^{3+}$-VO$^{••}$, Fe$^{2+}$-VO$^{••}$ and Ti$^{3+}$-VO$^{••}$ charged complexes in the SBFTi-x ceramics, and the interaction between them cause the relaxation time to diffuse in the form of bimodal, which also determine the spectral changes of $Z''$ and $M''$.[16]

$x$BiFeO$_3$-(1-$x$)Sr$_2$Bi$_4$Ti$_5$O$_{18}$ (SBFTi-x, $x=0, 0.1, 0.3$ and $0.5$) composite ceramics with six-layered Aurivilius structure were synthesized. Bi$^{3+}$ and Fe$^{3+}$ co-doped in A and B site cause the lattice distortion compared to SBTi ceramics, and it is the largest in SBFTi-0.3 ceramic. With the increasing of BFO content, the temperature dependence of the permittivity shows that the Curie temperature continuous increasing and the dielectric peak gradually broadened due to ups and downs of different composition and structure. Besides, the SBFTi-x ceramics show diffuse ferroelectric characteristics. The electrical structure in SBFTi-x ceramics become uniform and all samples show negative temperature coefficient characteristics. Space charge polarization and mixed relaxation processes were also found in SBFTi-x ceramics.

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