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Study of the Structural and Electrical Properties of Cr-Doped BiFeO3 Ceramic

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Abstract

Multiferroic BiFe$_{1-x}$Cr$_x$O$_3$ (x = 0.2 and 0.4) ceramics were synthesized in a single phase. The effects of Cr^{3+} substitution on the crystal structure, dielectric permittivity and leakage current were investigated. Preliminary X-ray structural studies revealed that the samples had a rhombohedral perovskite crystal structure. The dielectric constant ε' significantly increased while the dielectric loss tanδ was substantially decreased with the increase in Cr^{3+} substitution. The temperature effect on the dielectric properties exhibited an anomaly corresponding to magneto-electric coupling in the samples and was shifted to lower temperatures with the increase in Cr^{3+} substitution. The leakage current density also reduced in magnitude with the increase in the Cr^{3+} substitution.

Keywords

X-Ray Diffraction (XRD), Dielectric Properties, Leakage Current Density

1. Introduction

Materials with high dielectric permittivity values, so-called giant permittivity, reaching ε'-10^5, have been widely investigated because of their various applications in the microelectronic industry [1].

Multiferroic materials exhibit ferroic order parameters simultaneously, namely ferroelectricity, ferromagnetism and ferroelasticity, in the same phase [2] [3]. These materials have been widely studied in recent years because of their potential applications in new generations of memory devices, magnetic field sensors, etc. [4] [5]. However, the possibilities for room temperature single phase multiferroic materials are limited. Most of these materials have high ferroelectric Curie temperature T$_c$ and high magnetic transition temperature (Neél temperature T$_N$) [6] [7].

The main multiferroic oxide compounds are $BiFeO_3$, $BiMnO_3$ and $ReMnO_3$ (Re = Y, Ho, Lu). Among them, $BiFeO_3$ is one of the most investigated multiferroic materials, which belongs to the rhombohedral space group R3c, and transforms to the orthorhombic space group Pbnm at a ferroelectric Curie temperature T_c-1103 K. In addition, it shows typical G-type antiferromagnetic properties below its Neél temperature T_N-643 K [8] [9].

Although $BiFeO_3$ (BFO) materials show potential in several applications, some of their drawbacks still need to be resolved, such as large dielectric loss and high leakage current, which are induced by oxygen vacancy, non-stoichiometry and valence fluctuation of Fe ions at room temperature [2]. However, because of the higher leakage current in the bulk BFO, it was difficult to measure the ferroelectric properties of BFO at room temperature. The problem of higher leakage hinders not only the studies of the electrical properties of BFO but also the application of BFO in electrical devices. Oxygen vacancies in the BFO material are the major origin of the formation of Fe^{2+}, according to

$$V_O^X + 2Fe^{3+} \Leftrightarrow V_O^{\bullet\bullet} + 2Fe^{2+}$$

where $V_O^{\bullet\bullet}$ is the oxygen vacancy and V_O^X is the oxygen position [10]. Following the Le Chatelier principle [11], the concentration of Fe^{2+} is reduced if the content of Fe^{3+} is decreased. Therefore, substitution of rare-earth ions (La, Nd and Gd) at Bi^{3+} sites in BFO or transition-metal-ions (Mn, Cu and Co) at Fe^{3+} sites would control the formation of oxygen vacancies and reduce the concentration of Fe^{2+} in BFO [12] [13]. Among such ions, Cr doping BFO could improve the electrical properties and give lower leakage current than pure BFO [14].

In this work, we study the synthesis of BFO ceramics doped with Cr. The effect of Cr^{2+} substitution on structural and dielectric properties, and leakage current of BFO namely $BiFe_{1-x}Cr_xO_3$ ($x = 0.2$ and 0.4) ceramics is outlined in detail.

2. Experimental

Polycrystalline samples of $BiFe_{1-x}Cr_xO_3$ (x = 0.2 and 0.4) were synthesized by a solid-state reaction at a high temperature of 1273 K and a pressure = 7 GPa. A mixed powder of Bi_2O_3 (99.9%), Fe_2O_3 (99.9%) and Cr_2O_3 (99.9%) with stoichiometric proportions in a 1:1 mole ratio was mixed in an agar mortar for half an hour, then packed into a gold capsule ($\approx 4 \times 6\ mm^2$). It was then heated in a cubic anvil-type apparatus under 7 GPa at 1273 K for 1 hour [15]. X-ray diffractions (XRD) were carried out using a diffractometer with Cu-Kα source. The X-ray patterns were collected at an interval of 0.01˚. The structural parameters were refined by employing the Rietveld analysis of diffraction data in the 2θ range of 20˚ - 70˚. Dielectric permittivity measurements were carried out using an RLC meter in conjunction with a laboratory-made sample holder and a heating arrangement. Dielectric data were collected while heating in the temperature range from room temperature up to 773 K and using a frequency = 10 kHz. Leakage currents were measured by using a 4200-SCS semiconductor characterization system (Keithly).

3. Results and Discussion

Figure 1(a) shows the XRD patterns of calcined powder of $BiFe_{1-x}Cr_xO_3$ with x = 0.2 and 0.4 at room temperature.

All the peaks were indexed in single phase without any formation of a second phase with perovskite structure. Although calcination was performed, there were some impurity phases of $Bi_2Fe_4O_9$ and $Bi_{12}O_3$ as shown at $2\theta = 24.5^\circ$ - 30.1° for the samples, as reported by several authors [16]. The samples showed a rhomohedral structure with R3C spacing group and have been indexed as a hexagonal unit cell.

To further investigate the effect of increasing Cr content on the structure of $BiFe_{1-x}Cr_xO_3$, subtle XRD patterns with the strongest diffraction peaks of 2θ around 22˚ - 23˚ and 45.5˚ - 46.5˚ were obtained, as shown in **Figure 1(b)** and **Figure 1(c)**. The figure shows that when the Cr^{3+} substitution is increased, the position of peaks shifted towards the higher angle side as x increased, leading to a decrease in lattice parameters for x = 0.4. This was expected because the ionic radius of Cr^{3+} (0.615 Å) is smaller than that of Fe^{3+} (0.645 Å) [2] [15]. Thus, a distortion and deformation of the structure occurred when Fe^{3+} and Cr^{3+} ions were substituted at the B-site. The lattice parameter data are given in **Table 1**.

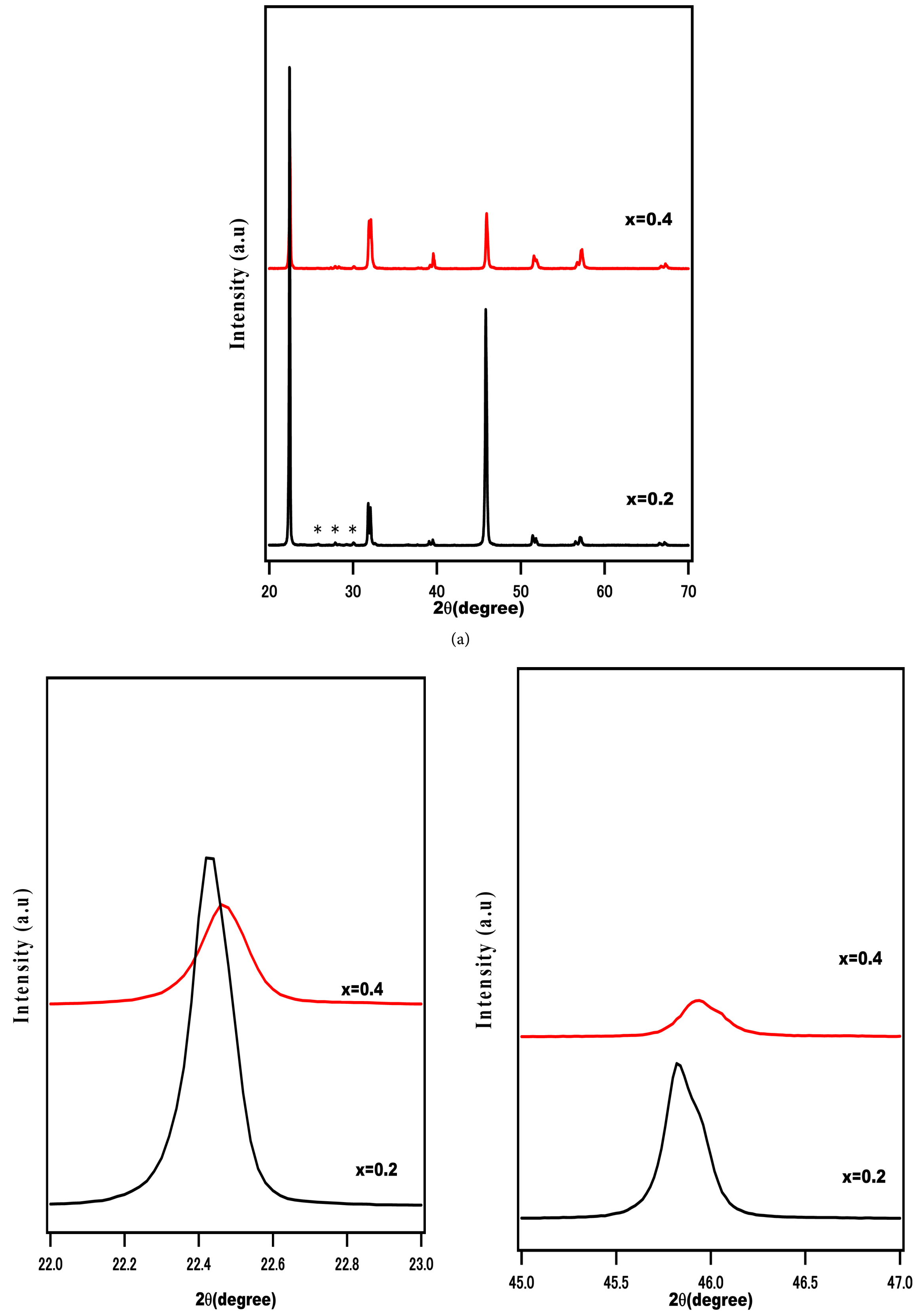
Figure 2 and **Figure 3** displays the temperature-dependent variation in dielectric constant ε' and dielectric loss $\tan\delta$ for $BiFe_{1-x}Cr_xO_3$ ceramics (x= 0.2 and 0.4) performed at 10 kHz. The dielectric constant for the two samples shows a continuous increase with elevating temperatures. A significant anomaly (plateau) was observed around 220˚C - 240˚C in the dielectric constant of the samples, which is consistent with other reported studies [17] [18] [19]. This anomaly (plateau) is attributed to the transient interaction between oxygen ion vacancies and Fe^{2+} and Fe^{2+} redox being responsible for the conductivity of the samples. The plateau range becomes narrower with the Cr^{3+} substitution, showing that the Cr^{3+} substitution decreases the oxygen vacancies, which in turn reduces in the concentration of Fe^{2+} in $BiFe_{1-x}Cr_xO_3$.

Thereafter, as shown in **Figure 2**, the dielectric constant increases rapidly with increasing temperature. The dielectric peak is observed in the samples (x = 0.2 and 0.4) at around 430˚C and 360˚C, respectively, which is above the Neél temperature. The Neél temperatures observed for x = 0.2 and for x = 0.4 are 242˚C and 170˚C, respectively [inset of **Figure 2(a)** and **Figure 2(b)**] as confirmed from our earlier magnetic study report [15].

This peak in the dielectric constant is attributed to a transformation from the antiferromagnetic order to the paramagnetic order, indicating an effect of disappearing magnetic order as compared to electric order, and attests to magneto-electric

Table 1. Lattice parameters of $BiFe_{1-x}Cr_xO_3$ (x = 0.2 and 0.4) ceramics.

Sample	a (Å)	c (Å)	c/a	V ($Å^3$)
x = 0.2	5.576	13.841	2.482	372.68
x = 0.4	5.563	13.773	2.475	369.12

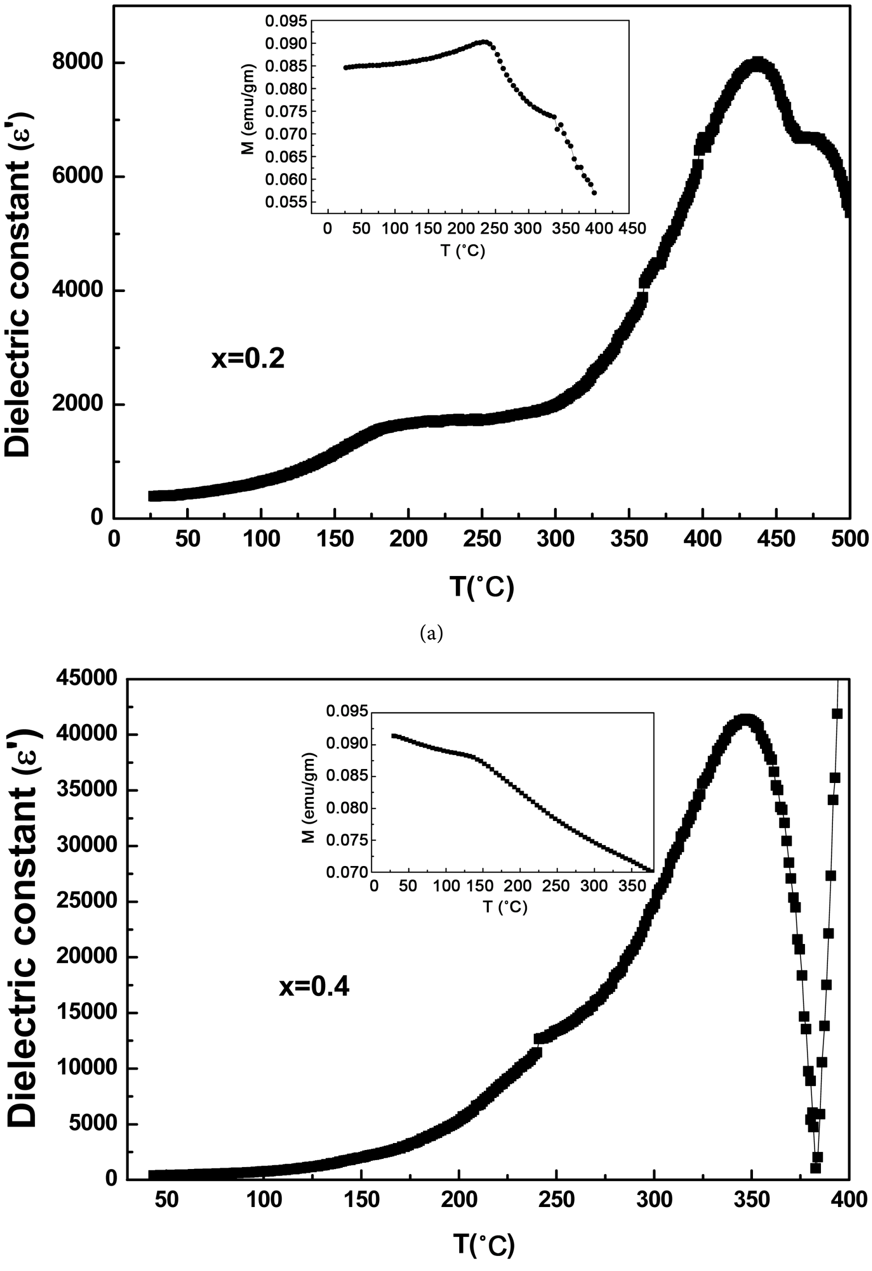


(a)

(b)

(c)

Figure 1. (a)-(c) X-ray diffraction pattern of $BiFe_{1-x}Cr_xO_3$ ceramic, x = 0.2 and 0.4.

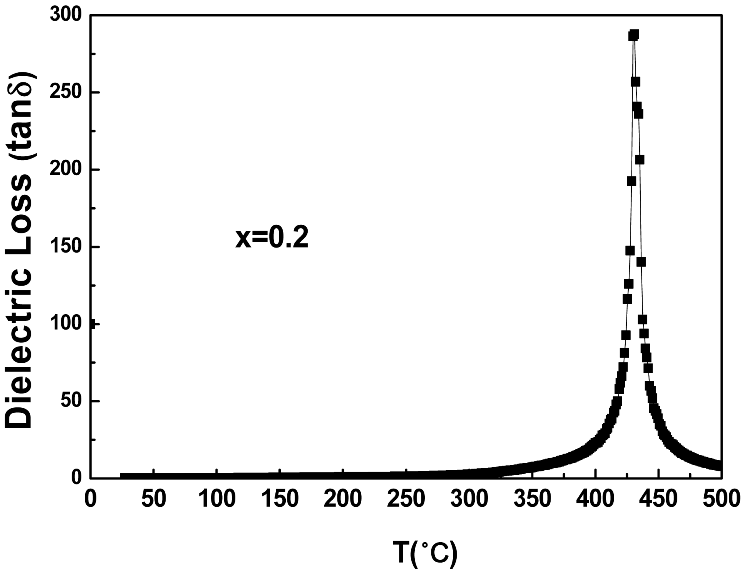


(a)

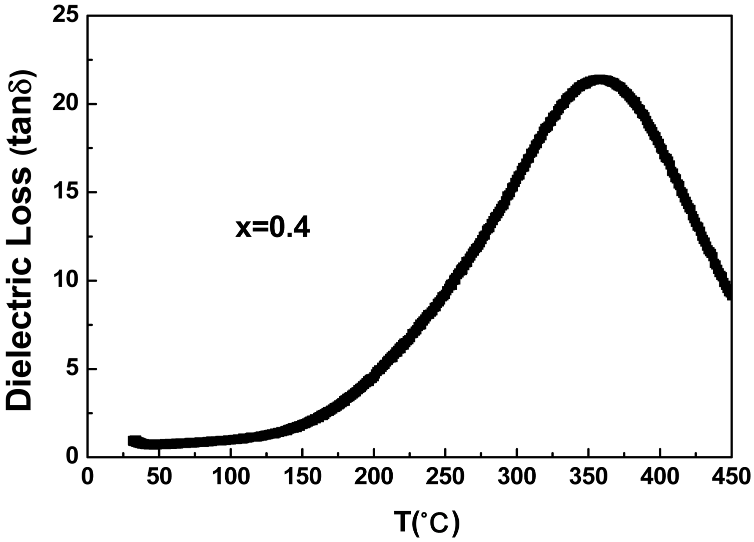
(b)

Figure 2. Temperature dependence of dielectric constant (ε') of $BiFe_{1-x}Cr_xO_3$ ceramic with x = 0.2 and 0.4 at 10 kHz.

coupling in the two samples. This type of anomaly near the Neél temperature has also been predicted by several studies [20]-[25]. **Figure 3(a)** and **Figure 3(b)** shows the variation in dielectric loss tan(δ) for $BiFe_{1-x}Cr_xO_3$ ceramics (x = 0.2 and 0.4). Further, as noted in the dielectric constant, anomalies are observed at 430°C and 360˚C for x = 0.2 and 0.4, respectively. In addition, the peaks in dielectric constant ε' and dielectric loss tan(δ) shifted toward a lower temperature with increased of Cr^{3+} substitution which indicates a decrease in the antiferromagnetic ordering temperature upon Cr^{3+} substitution.



(a)



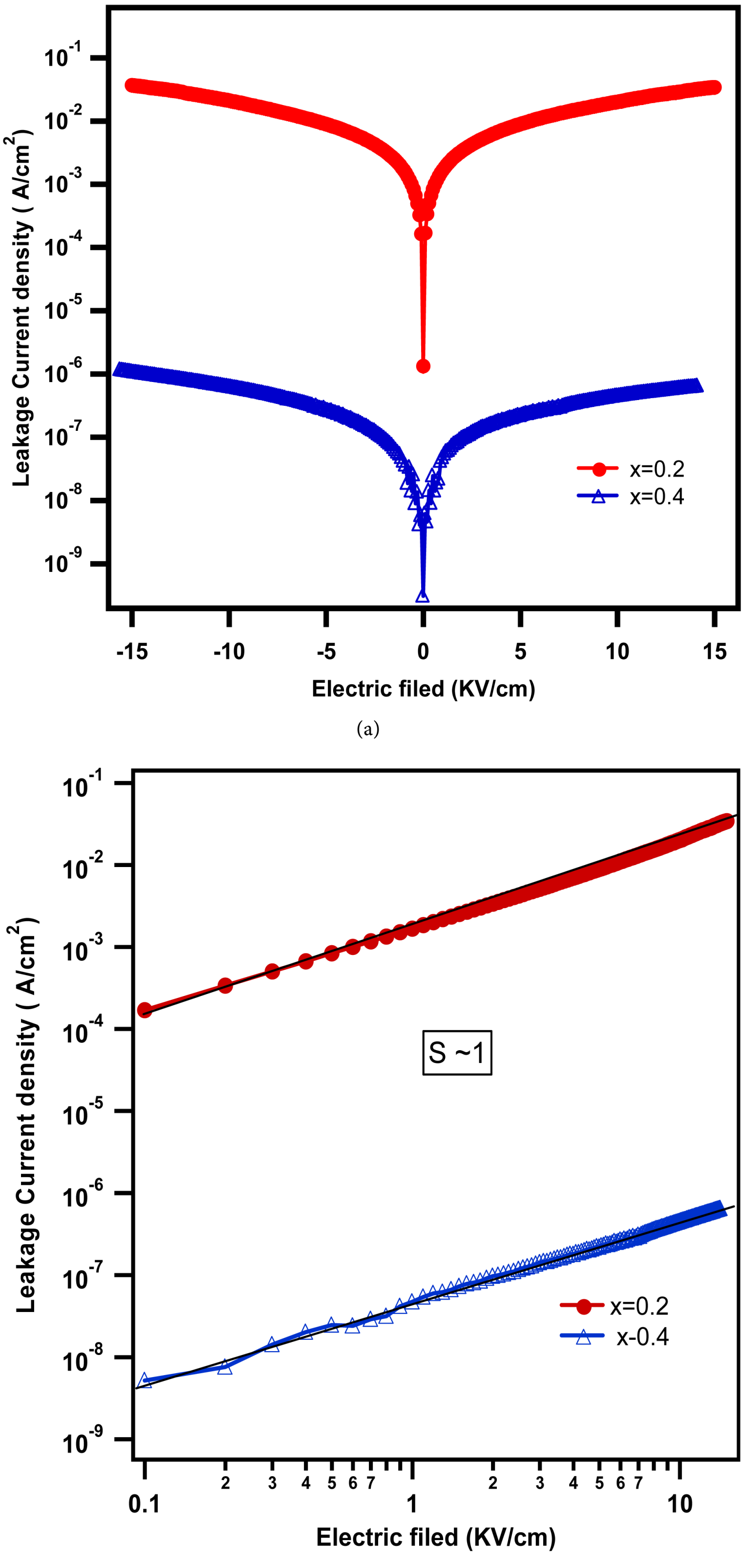
(b)

Figure 3. Temperature dependence of dielectric loss (tanδ) of $BiFe_{1-x}Cr_xO_3$ ceramic with x = 0.2 and 0.4 at 10 kHz.

The value of dielectric constant ε' increases while that of dielectric loss tanδ decreases with increasing Cr^{3+} substitution. This suggests that Cr^{3+} substitution can enhance the dielectric properties of $BiFe_{1-x}Cr_xO_3$.

The leakage current versus the electric field was measured at room temperature to study the conduction mechanism of $BiFe_{1-x}Cr_xO_3$ceramic. Figure 4(a) shows the current density as a function of the applied electric field, measured under a DC applied electric field.

The leakage current was recorded with both polarities of the applied voltage. There was no significant difference between leakage current measured with positive and negative applied voltages due to the symmetric electrodes in the



(a)

(b)

Figure 4. (a) Leakage current as a function of applied electric field; (b) Leakage current density versus electric field on a logarithmic scale for $BiFe_{1-x}Cr_xO_3$, x = 0.2, and 0.4 ceramic.

ferroelectrics-metal configuration. At the same applied voltage, the measured leakage current density of the $BiFe_{1-x}Cr_xO_3$ exhibited a reduction of approximately five orders with the increase in Cr^{3+} substitution from x = 0.2 to x = 0.4; this finding indicate a significant the improvement in reduction of leakage current density with Cr^{3+} substitution. The mechanism for leakage current reduction in the doped samples is complicated. Oxygen vacancies are one of them [26]. The reduction in $Fe^{3+}$and consequently Fe^{2+} is probably compensated by the substituted Cr^{3+} ion, which reduces the oxygen vacancies as mentioned above, thereby causing a reduction in leakage current density.

To better understand the conduction mechanism, we present a log(J) - log(E) plot in **Figure 4(b)**. As shown in **Figure 4(b)**, the relationships of the samples are almost linearly proportional. The slopes of the log (J) - log(E) plots are similarly close to 1, indicating that ohmic contact dominates the conduction mechanism in the applied field region [6].

4. Conclusion

In summary, the structural and electrical properties of $BiFe_{1-x}Cr_xO_3$ (x = 0.2 and 0.4) multiferroic ceramics synthesized by solid-state reaction at high pressure were investigated. The obtained $BiFe_{1-x}Cr_xO_3$ ceramic can be considered as a material of great dielectric permittivity that is very promising from the application perspective. XRD studies indicated that the crystal structure of the samples with x = 0.2 and 0.4 crystallized in a rhombohedral structure. In addition, the dielectric permittivity increased and dielectric loss decreased with increasing x. Anomalies were also observed in all samples at different temperatures corresponding to magneto-electric coupling. The leakage current decreased in magnitude with increasing x. The slopes of the logJ - log E were similar, indicating that ohmic contact prevailed. Thus the electric properties and leakage current could be improved by Cr^{3+} substitution. On the basis of these results, we conclude that Cr^{3+} substitution certainly helps in enhancing multiferroic properties and is a strong candidate for multifunctional applications.

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