High dielectric permittivity in Ca$_{1-x}$Bi$_x$Ti$_{1-x}$Cr$_x$O$_3$ ferroelectric perovskite ceramics

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Abstract
Polycrystalline structure of Ca$_{1-x}$Bi$_x$Ti$_{1-x}$Cr$_x$O$_3$ perovskite oxides were prepared by conventional solid state reaction with $x = 0.01, 0.03, 0.05, 0.1, 0.3$ and $0.5$. The crystal structure of the specimens changes with composition. The crystal structure for compositions up to $x \leq 0.1$ is similar to that of CaTiO$_3$ with $Pnma$ space group. When $0.1 \leq x \leq 0.3$, mixed phases in the specimens were observed and it changed to a rhombohedral structure ($R\bar{3}c$ space group) for $x \geq 0.5$. The dielectric constants and dissipation factors were measured at frequencies from 100 to 1 MHz. As a result, the dielectric constants were found to increase with increasing BiCrO$_3$ concentration. For $x = 0.3$, the dielectric constant at 1 kHz is higher than 600 000 for a sample sintered at 1300$^\circ$C for 5 h. The dielectric behaviors of these materials were contributed by orientational and space charge polarizations.

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1. Introduction
In 1943, CaTiO$_3$ with orthorhombic distortions of the perovskite structure was observed from X-ray diffraction by Naray-Szabo. It is paraelectric at room temperature, having dielectric permittivity above 180 and a dissipation factor ($\delta$) $\sim 10^{-3}$ at 1 kHz [1]. Generally, the dielectric properties have been improved by suitable substitutions in the perovskite oxides [2–4]. There are three types of substitutions in the perovskite oxides (ABO$_3$). Substitutions may be performed at the A site, the B site or both. Recently, extensive studies of the formation of perovskite oxides of the systems Ca$_{1-x}$M$_x$Ti$_{1-x}$M'O$_3$ (M = Y, Sr, Ba, Pb, M' = Co, Al, Fe, Cr) with rare earth elements were performed. This class of materials has become of importance and has been used in a number of electronic devices [5–8]. The replacement of Ca$^{2+}$ by high-valence ions creates additional positive charges, which are compensated by negative charges created from the replacement of Ti$^{4+}$ by low-valence ions leading to charge neutrality. From acceptor (La ions substituted into Ca site) and donor doping (Cr ions substituted into Ti site), it is found that doping can shift the Curie temperature.

BiCrO$_3$ is a multiferroic material [9]. Multiferroic magnetoelectrics are materials which are both ferroelectric and ferromagnetic in the same phase [10]. For example, they have a spontaneous magnetization which can be switched by an applied magnetic field, a spontaneous polarization which can be switched by an applied electric field. BiCrO$_3$ like the counterpart BiMnO$_3$ and BiFeO$_3$, is unstable in the cubic perovskite phase, with a structural instability driven by stereochemical activity of the Bi lone pair. This indicates that BiCrO$_3$ is stable against displacement of an isolated atom, and collective atom displacements are required to stabilize the distorted structure. Hence Cr$^{3+}$ ions will move to off-center positions which leads to strong polarization in the structure.

In the present work we investigated the stability of the perovskite phase in the Ca$_{1-x}$Bi$_x$Ti$_{1-x}$Cr$_x$O$_3$ system. Furthermore, phase relations and dielectric properties are presented in this paper.
2. Experimental

The compounds used in this investigation were prepared using a conventional powder-sintering technique, and starting materials with a purity at least 99% or higher. Solid solution oxides according to formula \( \text{Ca}_{1-x}\text{Bi}_x\text{Ti}_{1-x}\text{Cr}_x\text{O}_3 \) (\( x = 0.01, 0.03, 0.05, 0.1, 0.3, 0.5 \)) were prepared. The powders were mixed and ground with acetone in zirconium oxide ball mill for 24 h. The mixed powders were dried and calcined at 1000°C for 10 h. Finally, the calcined powders were reground and pressed into disks with diameter of 10–11 mm and thicknesses of 1–2 mm. The disks were sintered in air at 1200–1350°C for 5 h at a rate of 5°C/min before being cooled down to room temperature.

The phase-purity, structure and the lattice parameters of the samples were determined by X-ray power diffraction with Cu-K\(\alpha\) radiation at room temperature. The particle morphology and particle size were characterized by scanning electron microscopy (SEM). The density of sintered \( \text{Ca}_{1-x}\text{Bi}_x\text{Ti}_{1-x}\text{Cr}_x\text{O}_3 \) was measured using the Archimedes’ method in de-ionized water. The dielectric constants and dielectric loss were measured from 100 Hz to 1 MHz at room temperature using LCR (HP4284A) meter.

<table>
<thead>
<tr>
<th>Composition (x)</th>
<th>Lattice parameters (Å)</th>
<th>Crystal structure</th>
<th>Space group</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>( a ) ( b ) ( c )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.01</td>
<td>5.3844 5.4423 7.6508</td>
<td>Orthorhombic Pnma</td>
<td></td>
</tr>
<tr>
<td>0.03</td>
<td>5.3869 5.4529 7.6506</td>
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</tr>
<tr>
<td>0.05</td>
<td>5.3911 5.4486 7.6546</td>
<td>Orthorhombic Pnma</td>
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<tr>
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<td>5.3905 5.4560 7.6587</td>
<td>Phase mixture –</td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>5.3908 5.4571 7.6583</td>
<td>Phase mixture –</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>5.3905 – – –</td>
<td>Rhombohedral R3c</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2. Scanning electron micrographs of thermally etched surfaces with \( x \) (a) 0.01, (b) 0.03, (c) 0.05, (d) 0.1, (e) 0.3 and (f) 0.5 in the system \( \text{Ca}_{1-x}\text{Bi}_x\text{Ti}_{1-x}\text{Cr}_x\text{O}_3 \) sintered at 1280°C for 5 h.
3. Results and discussions

3.1. Crystal structure

The Ca\textsubscript{1-x}Bi\textsubscript{x}Ti\textsubscript{1-x}Cr\textsubscript{x}O\textsubscript{3} (x = 0.01, 0.03, 0.1, 0.3 and 0.5) perovskite oxide ceramics were formed with the same orthorhombic symmetry and the corresponding XRD pattern (Fig. 1) could be indexed similar to CaTiO\textsubscript{3} on the basis of space group Pnma. Because the BiCrO\textsubscript{3} structure is similar to that of BiFeO\textsubscript{3} it has a disordered perovskite structure with rhombohedral symmetry (R\textbar3c) at room temperature. For x ≥ 0.5 the structure of the ceramics changes from orthorhombic symmetry to rhombohedral symmetry [11,12]. The XRD patterns indicate that the intensity of the reflection increase with increasing x. The marked peaks for the BiCrO\textsubscript{3} phase indicate that the intensity increases with the x. However, the peaks shift and some of the weaker peaks corresponding to (1 0 3) and (1 1 3) of the orthorhombic structure [see marked peaks] tend to become reduced as x increases to 0.5. These results can be explained by the fact that partial substitution of Bi\textsuperscript{3+} (1.20 Å) and Cr\textsuperscript{3+} (0.615) ions for Ca\textsuperscript{2+} (1.32 Å) and Ti\textsuperscript{4+} (0.605 Å) ions, respectively can lead to an enhancement of the crystallinity and structural distortion.

The crystal system and lattice parameters of different compositions were calculated and are given in Table 1.

![Graph](image-url)
Silicon was used as the internal standard. As shown in Table 1, there are significant changes in the crystal structure and lattice parameters for the composition $x = 0.5$. The specimens with $0.1 \leq x \leq 0.3$ could be indexed as orthorhombic structure. When $0.1 \leq x \leq 0.3$, a mixture of phases is present in the specimens and the structure changed to the rhombohedral as type for $x \geq 0.5$. Moreover, initially the lattice parameters increase only slowly for $x \leq 0.3$. Beyond this concentration larger changes become apparent due to the structural distortion and phase transition.

Scanning electron microscopy (SEM) pictures of the various samples (0.01, 0.03, 0.05, 0.1, 0.3 and 0.5) are shown in Fig. 2a–f, respectively. All of samples have a dense structure. By comparing Fig. 2a–c, it can be seen clearly that the grains were significantly ledged for doping concentration below 0.1. The ledges are attributed to two phases: CaTiO$_3$ and BiCrO$_3$ forming an interface with different crystal structures. In the sintering process, for lower doping levels, an atom attempting a jump will, therefore, be come unstable and be forced back to its original position. It can thus be seen that continuous growth at the above type of interfaces will be very difficult. A way of avoiding the difficulties of continuous growth encountered in the above case is provided by the ‘ledge’ mechanism shown in Fig. 2a–c [13].
For high doping levels, it can be seen clearly that the ledges tend to disappear. The disappearance is attributed to the fact that high doping concentrations involve a phase transition from unstable orthorhombic symmetry of CaTiO$_3$ to stable rhombohedral symmetry of BiCrO$_3$. The corresponding final equilibrium shape of the crystals is shown in Fig. 2e and f.

### 3.2 Dielectric behaviors

Plots of the dielectric constants ($\varepsilon$) and dissipation factors ($D$) versus temperature at different sintering temperature and measured at $1 \text{ K}$ and $100 \text{ Hz}$ for samples with concentration $x = 0.1$ are shown in Fig. 3a and b and Fig. 3c and d, respectively. It was found that for all the samples the dielectric constant increased with increasing temperature. There are two peaks in the dissipation factor curves at 270 and 450 K, respectively. These two peaks are attributed to different structure (Pnma or $R\overline{3}c$) in the material with concentration of $x = 0.1$. When the doping concentration is higher or lower than $x = 0.1$, the dissipation factor curve have only one peak as shown in Fig. 4b and d. On the other hand, the value of the dielectric constant remains constant initially with increasing temperature up to a particular temperature $T_a$ [14]. Beyond this temperature it starts to increase rapidly resulting in the occurrence of dissipation factor peaks at temperatures near $T_a$ as shown in Fig. 3b. However, the BiCrO$_3$ structure has a first-order phase transition accompanied by thermal hysteresis observed at around 400 K [9]. Hence, the appearance of the other peaks may be caused by the phase transition of the BiCrO$_3$. The peaks lead to shift to lower temperature when lowering the measuring frequency down to $100 \text{ Hz}$, as shown in Fig. 3d.

Fig. 4 shows the variation of dielectric constants and dissipation factors ($D$) as a function of temperature at $1 \text{ kHz}$ for $x = 0.05, 0.1, 0.3, 0.5$. When samples were sintered at $1280 \degree\text{C}$ for $5 \text{ h}$, the dielectric constants increased with increasing doping concentration. For $x = 0.1$, a peak in the dissipation factor curve occurs near the temperature $T_a$ as shown in Fig. 4a and b, respectively. When the samples were sintered at $1300 \degree\text{C}$ for $5 \text{ h}$, the dielectric constants for $x = 0.3$ are higher than for $x = 0.5$. This phenomenon may be caused by the large distortion of the octahedral site resulting from the high doping level and the high sintered temperature.

During sintering the sample at high temperature, a slight amount of oxygen is lost according to the reaction:

$$\text{O}_2 \leftrightarrow 2\text{O}^+ + 2e^-$$

where all the symbols have been used in accordance with Kroger–Vink notation of defects. The oxygen vacancies exist in doubly ionized state above 550 $\degree\text{C}$. Below 550 $\degree\text{C}$, oxygen vacancies exist as singly ionized defects as $V^+_O$ [14,15] according to the reaction:

$$V^+O + e^- \leftrightarrow V^O$$

These oxygen vacancies act as intrinsic donors. Electric release in reaction (1) during the sintering process induces trivalent Bi$^{3+}$ ion to substitute for Ca$^{2+}$ acting as extrinsic donors. Similarly trivalent Cr$^{3+}$ ion substitutes for Ti$^{4+}$ acting as extrinsic acceptor. The overall charge neutrality condition requires that the sum of charges on the positive and negative charge defects should be equal [16]. Therefore, these $V^O$ and $V^+O$ combine Cr$^{3+}$ to form dipoles of the type $(\text{Cr}^{3+} - V^O)$ or $(2\text{Cr}^{3+} - V^+O)$ due to Coulombic attraction. Another process, which may occur is the hopping of holes among $V^+_O$ and $V^{2+}_O$ which will again lead to a change in orientation of the dipoles [17]. In addition, when CaTiO$_3$ is doped with BiCrO$_3$ this may cause a distortion of the octahedral sites in the structure. As a result, the distorted octahedrals sites are coupled together and a very large spontaneous polarization can be achieved at the transition temperature. This large spontaneous polarization and orientation polarization will lead to a large dielectric constant as shown in Fig. 5. At low frequencies such as 100 Hz and 1 kHz, the dielectric constants are higher than 600,000 at 400 K. This behavior is due to the fact that at low frequency the dipoles are able to follow the applied field whereas at higher frequency they are not. Therefore, the dielectric behaviors of these materials is at contributed to orientation and space charge polarizations.

### 4. Conclusions

The Ca$_{1-x}$Bi$_x$Ti$_{1-x}$Cr$_x$O$_3$ ceramic has a distorted perovskite structure. For $x < 0.1$, the crystal structure of the samples is similar to CaTiO$_3$ (orthorhombic) with $Pmmn$.
symmetry. When the concentration is higher than 0.1, the crystal structure changes from orthorhombic symmetry to rhombohedral symmetry with space group $R\bar{3}c$ of BiCrO$_3$. For $x = 0.1$ the dissipation factor ($D$) curve shows two peaks at 270 K and 400 K, respectively. These two peaks are attributed to different structures ($Pnma$ or $R\bar{3}c$) in the material. The Ca$_{1-x}$Bi$_x$Ti$_{1-x}$Cr$_x$O$_3$ ceramics possess simultaneously large spontaneous polarization and orientation polarization. The value of the dielectric constant is about 140 000 at room temperature with a low dissipation factor, as obtained for the sample with $x = 0.3$ sintered at 1300 °C for 5 h and measured at 100 Hz–1 kHz.

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References