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Ferroelectric properties of $Bi_{4-x}Ce_xTi_3O_{12}$ ($0<x<4$) thin film array fabricated from $Bi_2O_3/CeO_2/TiO_2$ multilayers using multitarget sputtering

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We fabricated a ferroelectric $Bi_{4-x}Ce_xTi_3O_{12}$ thin film library by solid-state mixing of $Bi_2O_3/CeO_2/TiO_2$ multilayers using a multitarget rf magnetron sputtering equipped with an automated shutter. Polarization-electrical field and the structure are mapped as a function of Ce content (x) from 0 to 4. The remnant polarization decreases as Ce content increases, and at $x \geqslant 0.8$, $Bi_{4-x}Ce_xTi_3O_{12}$ samples exhibit a paraelectric property due to the formation of impurity phases such as $Bi_2Ti_2O_7$ and CeO_2. Among the thin film samples of the library, $Bi_{3.85}Ce_{0.15}Ti_3O_{12}$ exhibited the largest remnant polarization of 13.0 $\mu C/cm^2$. *© 2008 American Institute of Physics*. [DOI: 10.1063/1.2841039]

Ferroelectric materials that can be used as a capacitor in the ferrolectric random access memory (FeRAM) have been studied intensively.[1–5] Perovskite metal oxides including $Pb(Zr,Ti)O_3$ (PZT),[2,3] $SrBi_2Ta_2O_9$ (SBT),[4] and $(Bi,La)_4Ti_3O_{12}$ (BLT) (Ref. 5) have been suggested as candidate materials for FeRAM capacitor. Among these materials, bismuth layer-structured ferroelectrics, including SBT and BLT, have attracted attention because of their fatigue-free properties, in contrast to PZT which has a fatal problem in fatigue endurance due to interdiffusion between Pb and Pt electrodes. Recently, enhanced remnant polarizations were reported by substituting lanthanide group metals for the Bi sites of $Bi_4Ti_3O_{12}$.[6–9] Though the improved remnant polarization is largely dependent on the amount of substituted atom, systematic study on the composition dependence of P_r was not carried out in the entire range of composite because of the large number of experiments.

High-throughput synthesis and analysis methods, which have recently been applied to the discovery and optimization of a number of functional materials, allowed us to investigate the properties of multicomponent materials in a reasonably short time.[10–19] In previous studies, we reported the effect of La content on the remanent polarization of $Bi_{4-x}La_xTi_3O_{12}$ and $Bi_{3.75}La_xCe_{0.25-x}Ti_3O_{12}$ using the combinatorial methodology.[20,21]

We fabricated the $Bi_{4-x}Ce_xTi_3O_{12}$ (BCT), ($0<x<4$) thin film library and investigated the effect of Ce content on the remanent polarization and phase transition of BCT in this study.

We used a multitarget sputtering system (SUNICOAT-524, manufactured by Sunic System Co. Ltd.) with three ceramic targets of Bi_2O_3, TiO_2, and CeO_2 (purity =99.999%, diameter=4 in.) to synthesize the combinatorial thin film library of $Bi_{4-x}Ce_xTi_3O_{12}$. TiO_2 was deposited first on a (111) $Pt/TiO_2/SiO_2/Si$ substrate. In order to vary the chemical composition of Bi/Ce, different amounts of Bi_2O_3 and CeO_2 were deposited by varying the deposition time by moving the automated shutter back and forth over the substrate. The motion of the shutter was synchronized with the plasma generation such that a thickness-gradient "wedge" was created on the substrate for each deposition. Then, TiO_2 was deposited to form a sandwich structure of $TiO_2/Bi_2O_3/CeO_2/TiO_2$, as shown in Fig. 1(a). This procedure was repeated 16 times to obtain a BCT library of 250 nm thickness.

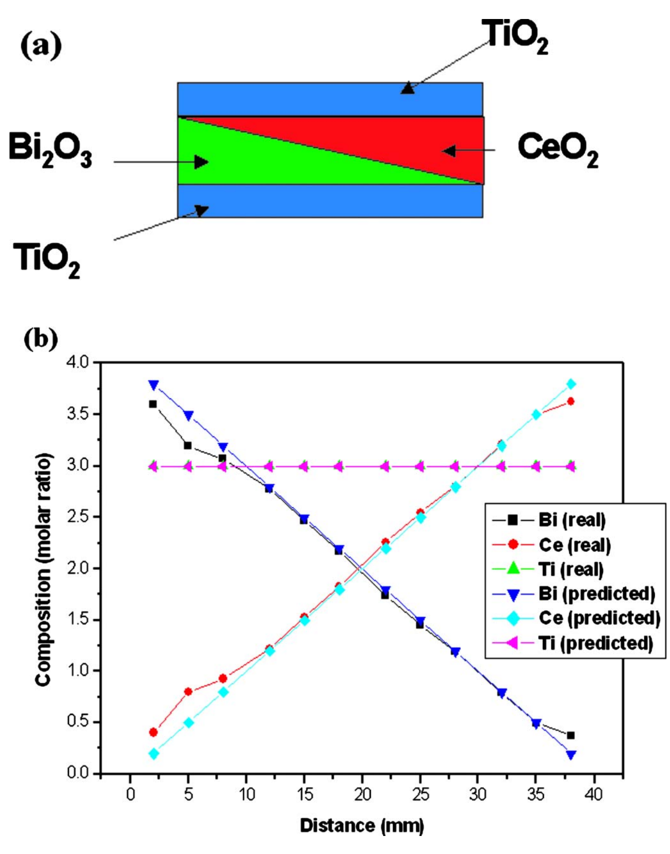

FIG. 1. (Color online) (a) The schematic diagram of $Bi_{4-x}Ce_xTi_3O_{12}$ thin film array from $TiO_2/Bi_2O_3/CeO_2/TiO_2$ multilayers using the multitarget sputtering system. (b) The chemical composition of $Bi_{4-x}Ce_xTi_3O_{12}$ in the x direction. These results were measured by WDS.

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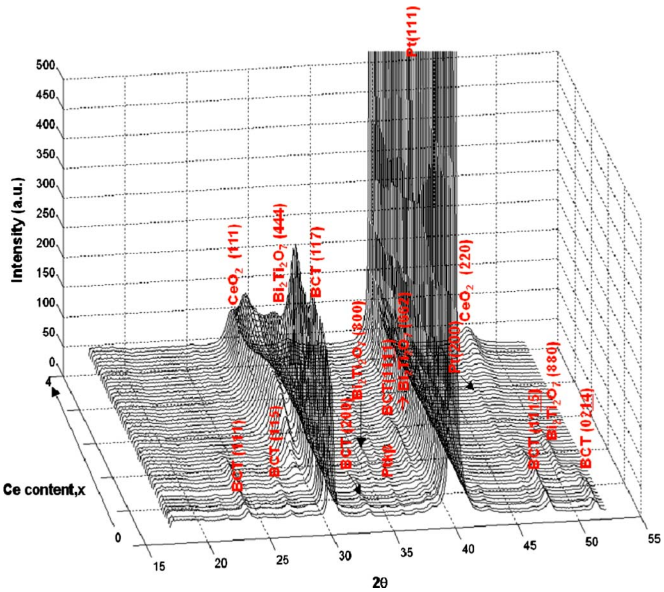

FIG. 2. (Color online) The microbeam x-ray diffractogram of $Bi_{4-x}Ce_xTi_3O_{12}$ as a function of Ce content x.

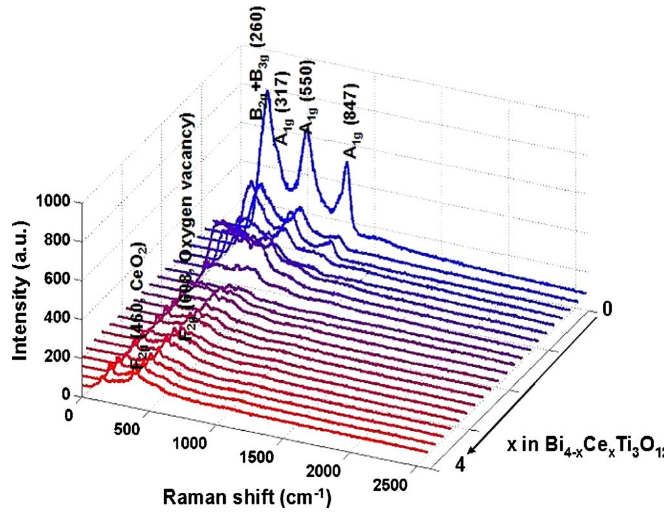

FIG. 3. (Color online) The micro-Raman spectra of $Bi_{4-x}Ce_xTi_3O_{12}$ as a as a function of Ce content x (laser power of 40 mW and detection time of 10 s/sample).

The substrate temperature was maintained at 300 °C during deposition for efficient intermixing. A gas mixture of Ar and O_2 [$Ar/O_2=3:1$, total flow rate=20 SCCM (SSCM denotes cubic centimeter per minute at STP)] was introduced to suppress the formation of oxygen vacancies during the deposition. The chamber pressure was maintained at 5×10^{-3} Torr. The system was initially pumped down to 5×10^{-6} Torr. The as-prepared thin film library was kept at 400 °C for 1 h under O_2. Then they were postannealed at 700 °C for 1 h under O_2 atmosphere to crystallize them completely.

Figure 1(b) shows the variation of x in the BCT thin film array along the z direction. Being measured by wavelength dispersive spectroscopy (WDS), (W filament, 10 keV), x varied linearly from 0 to 4 when z increased from 0 to 40 mm. A small discrepancy between the actual and intended composition near both ends of the library is attributed to the shadow effect caused by the thickness of shadow mask which was used to predefine the shape and size of thin film library.

A scanning x-ray microdiffractometer (GADDS D8 DISCOVER, Bruker-AXS) was used to characterize the crystal structure of the library with 50 BCTs having different Ce contents. As shown in Fig. 2, the structure is dependent on the Ce content x and the homogeneous BCT phase is present when x is less than 0.8. When x is greater than 0.8, new peaks appeared from $Bi_2Ti_2O_7$ including the (880) peak at 49.7°. When x is increased to 2, $Bi_2Ti_2O_7$ peaks disappeared and new peaks were observed at 28.6° and 47.7°, which are the (111) and (220) peaks of CeO_2, respectively. These results show that a pure BCT phase exists only when x is less than 0.8 and other phases become dominant when x is greater than 0.8.

We used a micro-Raman system (Dongwoo Optron Co. Ltd.) to characterize Ti–O internal vibration mode in TiO_6 and the results are shown in Fig. 3. To obtain the Raman spectrum, an Ar laser with 488 nm (laser power of 40 mW) was incident on the library and scanned along the z direction by a computer program. In BCT, the extent of distortion of TiO_6 octahedra determines remnant polarization,[21] and Raman spectroscopy is the best method in analyzing the TiO_6 structure. Three peaks were observed at 260, 550, and 847 cm^{-1}, which are assigned to the internal angle bending, combination of stretching and bending, and another stretching vibrations, respectively.[22,23] Among the peaks originated from the Ti–O bond, the peak at 847 cm^{-1} was focused on as the intensity of this peak is a good indicator for remnant polarization as shown in our previous report.[20] The Raman peak intensity is proportional to $(\int \psi^*_{v'} \alpha \psi_{v''} d\tau)^2$, where $\psi_{v'}$ and $\psi_{v''}$ are wave functions of the upper and lower vibrational quantum states, respectively. $d\tau = dxdydz$, where x, y, and z are the nuclear coordinates in the molecular frame and α is the polarizability.[24] Thus, strong peak intensity indicates large polarization based on $\mu = \alpha E$, where μ is the induced dipole moment and E is the electric field of the incoming radiation. The intensity of the peak at 847 cm^{-1} decreased with increasing x and disappeared when x was 0.8, indicating the decrease in remanent polarization. When x was greater than 0.8, new peaks were observed at 205 and 460 cm^{-1} which were assigned to CeO_2. A new band appeared at 608 cm^{-1} due to the oxygen vacancies in CeO_2.[25]

Figure 4 shows $2P_r$ values of the P-E characteristic as a function of Ce molar contents by using RT 66A equipment at applied voltage of 15 V. According to the results, in the range of $x \leq 0.8$, we observed the ferroelectric property in the library and $Bi_{3.85}Ce_{0.15}Ti_3O_{12}$ has the largest remnant polarization, 13 $\mu C/cm^2$. This is lower than previously reported value; however, importantly, we can observe the trend of P-E characteristics as a function of Bi/Ce simultaneously. In this compositional range, the remnant polarization decreased as the Ce content increased. This is similar to the intensity variation of Ti–O stretching mode, as shown in the BLT study, indicating that the micro-Raman spectroscopy is a useful method in analyzing ferroelectric combinatorial libraries.

In summary, we fabricated a BCT thin film library in the range of Ce content between 0 and 4 from $TiO_2/Bi_2O_3/CeO_2/TiO_2$, and found that it is possible to obtain a linear compositional gradient over the substrate by using an automated shutter. The largest $2P_r$ of 13 $\mu C/cm^2$ was obtained in $Bi_{3.85}Ce_{0.15}Ti_3O_{12}$. Micro-Raman spectros-

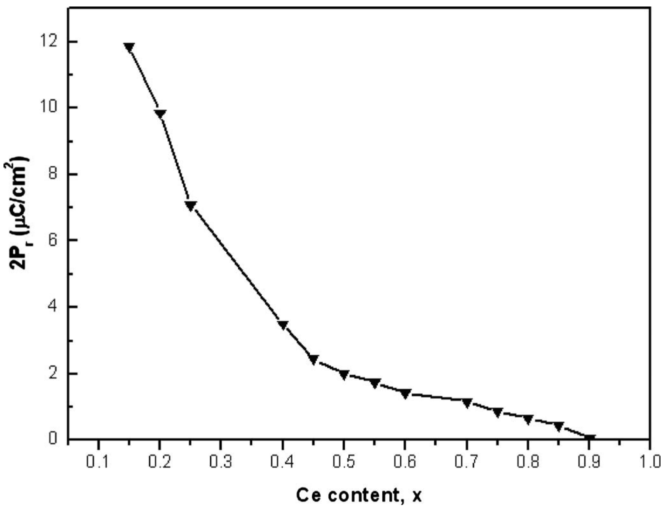

FIG. 4. The remnant polarization of $Bi_{4-x}Ce_xTi_3O_{12}$ as a function of Ce content x at an applied voltage of 15 V.

copy results showed that the intensity of 847 cm^{-1} is a good indicator for ferroelectric properties.

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