X-ray diffraction and Raman scattering study of $SrBi_2Ta_2O_9$ ceramics and thin films with Bi_3TiNbO_9 addition

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Good ferroelectric properties have previously been reported for both the $(1-x)SrBi_2Ti_2O_9-xBi_3TiNbO_9$ bulk ceramics and thin films. In this work, x-ray diffraction and Raman scattering were used to investigate the effect of the incorporation of Bi_3TiNbO_9 into $SrBi_2Ta_2O_9$ bulk ceramics and thin films. A better crystallization, larger grain size and larger displacement of the Ta–O(4) or Ta–O(5) ions are the origin for the good ferroelectric properties of $(1-x)SrBi_2Ta_2O_9-xBi_3TiNbO_9$ with $x=0.3-0.4$. © 2001 American Institute of Physics. [DOI: 10.1063/1.1421642]

Ferroelectric thin films have attracted considerable attention due to their potential applications in ferroelectric non-volatile random access memories (FeRAMs). $SrBi_2Ta_2O_9$ (SBT) has been reported to be one of the best candidates for FeRAMs because it exhibits good hysteresis behavior, almost no fatigue on Pt electrodes, lower leakage current, and long data retention time.[1] However, due to the high processing temperature ($>700\,°C$), relatively low remanent polarization (P_r), and low Curie temperature (T_c) of SBT films, the integration of SBT thin films with silicon technology has been delayed. For high density applications, the ferroelectric films need to be deposited directly on polysilicon, and this requires a low temperature process to ensure good interfacial properties. It is expected that with the incorporation of materials with high P_r and T_c such as Bi_3TiNbO_9 (abbreviated as BTN, $2P_r=27.7\,\mu C/cm^2$, $T_c=1223\,K$) into SBT will give a solid solution with higher P_r and T_c than SBT. Moreover, the solid solution may be processed at lower temperature. Zhang *et al.*[2] have fabricated complete solid solutions in the $SrBi_2Ta_2O_9–Bi_3TiNbO_9$ (SBT-BTN) system with a general formula of $(1-x)(SrBi_2Ta_2O_9)-xBi_3TiNbO_9$ $[(1-x)SBT-xBTN]$ successfully and have found that T_c increases with x. Ryu *et al.*[3] reported that thin film of the solid solution $(1-x)SBT-xBTiTaO_3$ $[(1-x)SBT-xBTT]$ fabricated by a modified metalorganic solution deposition technique showed highly improved properties. In particular, the film with $x=0.3$ has a large P_r and a well-defined ferroelectric $P-E$ hysteresis loop even at an annealing temperature of $650\,°C$. The ferroelectric property was significantly improved compared to $SrBi_2Ta_2O_9$, which has no appreciable polarization charge when annealed at $650\,°C$. Also, this kind of film shows good performance with respect to fatigue, re-

tention and leakage current. The improved ferroelectric property makes the solid-solution thin films attractive for high density integrated memory devices.[3]

However, the mechanism behind the improved ferroelectric properties of $(1-x)SrBi_2Ta_2O_9-xBi_3TiTa(Nb)O_9$ has not been elucidated. Vibrational studies can give the information about the displacements of the atoms or ions, some of which are related to the polarization of the material. The results of Liu *et al.*,[4] Zou *et al.*,[5] and Kojima *et al.*[6] indicate that Raman scattering is a useful tool for exploring the microscopic origin of the ferroelectricity of materials. In this letter, x-ray diffraction and Raman scattering spectra in bulk ceramics and thin films of $(1-x)SBT-xBTN$ at various x values are presented first and then used to analyze the change of the ferroelectric behaviors with x.

Stoichiometric mixtures $(1-x)SBT-xBTN$ with different x values (0, 0.2, 0.4, 0.6, 0.8, 1) were prepared. $SrCO_3$, Bi_2O_3, Ta_2O_5, TiO_2, and Nb_2O_5 were used as the starting materials, and the ceramic samples were prepared using conventional ceramic technology.[2] Films of $(1-x)SBT-xBTN$ solid solutions with various x values (0.1, 0.3, 0.4, 0.6, 0.8, 1) were prepared by a modified metalorganic solution deposition technique at room temperature using an alkoxide–carboxylate precursor solution. Details of the fabrication process of the thin films have been published elsewhere.[3,7]

X-ray diffraction measurements were performed using a Rigaku DMAX-A diffractometer with Cu $K\alpha$ radiation, $\lambda=1.54\,Å$. Raman scattering spectra were obtained using a Jobin–Yvon Ram-2 Infinity Micro-Raman System. Ferroelectric measurements were performed using a Radiant Technology RT-6000 system.

Figure 1 shows the x-ray results for ceramics (a) and thin films (b) at various x values. For the ceramics, the strongest (200) and (115) diffraction lines were observed at $x=0.4$ [Fig. 1(a)]. A strong (115) diffraction line was also observed in the thin film with $x=0.3$ [Fig. 1(b)]. Since the polarization
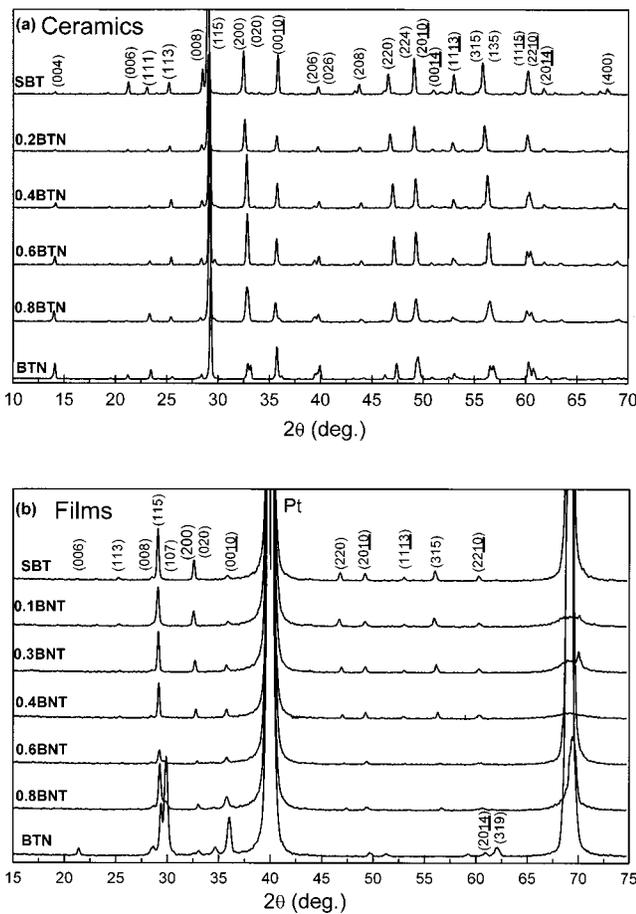
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FIG. 1. XRD θ–2θ curves of $(1-x)$SBT–xBTN solid solutions for different x; (a) for ceramics, and (b) for thin films.
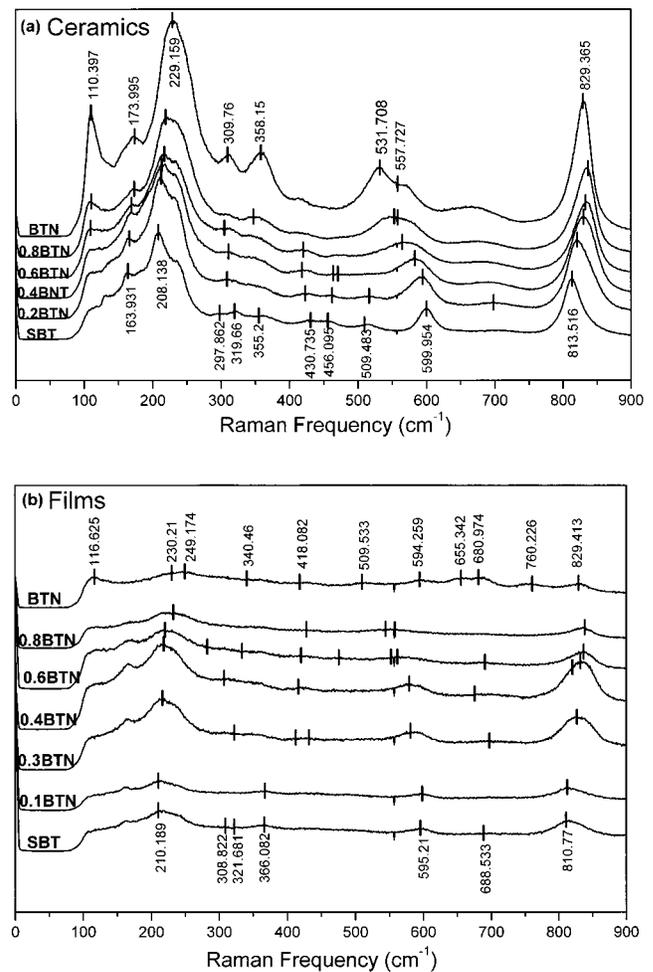

FIG. 2. Raman spectra for $(1-x)$ SBT–xBTN solid solutions for different x; (a) for ceramics, and (b) for thin films.

lies along the *a*-axis direction in this kind of materials,[8,9] the (200) and (115) orientations favor the *a*-domain formation in the thin film. Table I gives the measured P_r and E_c values in our ceramics with different x. The maximum P_r ($2P_r \approx 14 \, \mu\text{C/cm}^2$) is obtained at $x=0.4$ and large P_r ($2P_r \approx 12 \, \mu\text{C/cm}^2$) was also obtained in the thin film with $x = 0.4$. Ferroelectric measurements by other workers also showed that the largest P_r was obtained in both ceramics and thin films of $(1-x)$SBT–xBTN at about $x=0.3$–0.4.[3]

The Raman spectra in the spectral range 80–900 cm^{-1} for $(1-x)$SBT–xBTN ceramics and thin films at various x are shown in Figs. 2(a) and 2(b). At $x=0$, Raman bands around 100, 163, 210, 297, 355, 430, 600, and 813 cm^{-1} are observed in the ceramic materials. Due to the limitation of instrument, Raman bands of frequencies lower than 80 cm^{-1} are not observed. The incorporation of BTN into SBT affects the position and width of the bands significantly. The 163 cm^{-1} band is associated with the vibration of the Ta^{5+} ion along the *z* direction (TO mode A_{1g}). The band shifts to a

TABLE I. P_r and E_c in $(1-x)$SBT–xBTN ceramics are shown.

	P_r ($\mu\text{C/cm}^2$)	E_c (kV/cm)
SBT	2.32	34.54
0.8SBT–0.2BTN	3.98	65.37
0.6SBT–0.4BTN	6.88	88.62
0.4SBT–0.6BTN	2.67	63.62
0.2SBT–0.8BTN	2.24	67.75

higher frequency with increasing x as Ta^{5+} is progressively replaced by the lighter Nb^{5+} or Ti^{4+} ions. The 210 cm^{-1} band represents the TO mode of SrO with a rock salt structure.[6,10] Its intensity increases as x increases. The peak at about 600 cm^{-1} is associated with the internal vibration of the TaO$_6$ octahedron and the one at about 813 cm^{-1} is also related to the vibration of the TaO$_6$ octahedron. However, the oxygen ions contributing to these two bands are different. The vibration of the oxygen ion (O$_2$) at the apex of the TaO$_6$ octahedron gives rise to the 600 cm^{-1} band (E_g), while the vibration of oxygen ions (O$_4$, O$_5$) in the Ta–O plane gives rise to the 813 cm^{-1} band (E_g). With increasing x, the 600 cm^{-1} peak exhibits very little change in intensity but shifts to a lower frequency. Previous workers have found a downshift in frequency at 537 cm^{-1} peak in BTN when the composition is varied,[11,12] i.e., a softening was induced by changing the composition. For the $(1-x)$SBT–xBTN thin film at $x = 0$, bands are observed at 100, 163, 210, 600, and 813 cm^{-1} [Fig. 2(b)]. Comparing the Raman bands in ceramics and films, the Raman bands in thin films are broader than those in the ceramic materials with the same content x. This may indicate that there are more defects and a higher stress in the thin films.[11]

Figure 2 shows that, for most of the Raman bands, the width increases between $x=0$ and 0.6 and then decreases between $x=0.6$ and 1 for the ceramics, and increases be-

tween $x=0$ and 0.4 and decreases between 0.6 and 1 for the films. The materials at small x or large x are nearly single-phase materials, so it is understandable that their bandwidths are less than that of the materials with $x=0.5$, which is the mixture of two phases (SBT, BTN). The defects in the materials and the differences in ion mass between Sr and Bi in the A-perovskite sites and between Ta, Ti, and Nb ions in the B-perovskite sites are responsible for the increase in the Raman bandwidth.[11]

In $SrBi_2Ta_2O_9$ with the $A2_1am$ orthorhombic symmetry, the a axis is the polar axis. Atomic displacements along the a axis from the corresponding positions in the parent tetragonal ($14/mmm$) structure cause the spontaneous ferroelectric polarization. Displacements along the b and c axes, in contrast, cancel each other out due to the presence of glide and mirror planes, respectively, thus they do not contribute to the total polarization. Rae *et al.*[8] reported that the polarity can be quite well described as a movement of the Ta–O(4) and Ta–O(5) ions relative to the Bi and O(3) ions of the Bi_2O_2 layer with an additional movement of Ta relative to O(4) and O(5). Shimakawa *et al.*[9] suggested that large atomic displacements of Bi^{3+} in the Bi_2O_2 layer and of $O(5)^{2-}$ in the TaO_6 octahedron play an important role in the large ferroelectric spontaneous polarization of SBT. Although the displacements of Ta^{5+} and O^{2-} ions in the TaO_6 octahedron contribute to the total polarization oppositely, the net polarization caused by the distortion of the TaO_6 octahedron enhances the total ferroelectric polarization. Correspondingly, in our case the Raman spectra show that the frequencies (a) and intensities (b) of the 163, 213, 600, and 813 cm^{-1} bands in both the ceramics and the films change with x as shown in Figs. 3 and 2(b), respectively. The 813 cm^{-1} band, which is associated with the vibration of the Ta–O(4) or Ta–O(5) ions, is responsible for the spontaneous polarization in SBT. The frequency and intensity of the 813 cm^{-1} band increase with x ($x=0-0.4$) in both the ceramics and the films. The intensity of the 813 cm^{-1} band has a maximum at about $x=0.3-0.4$ [Figs. 3(b) and 2(b)]. Obviously, a large displacement of the Ta–O(4) or Ta–O(5) ions corresponding to a large polarization has been induced by the addition of 30%–40% BTN. With increasing BTN content, especially at $x \geq 0.6$, the distortion in the octahedron and the Bi–O plane increases, so the SBT structure gradually changes to the BTN structure. The increased distortion gives rise to a higher intensity of the 813 cm^{-1} band in the ceramics at $x>0.6$ shown in Fig. 3(b), and also in the thin films at $x>0.8$ [Fig. 2(b)].

In conclusion, x-ray diffraction and Raman scattering were used to investigate the origin of the increased ferroelectricity in ceramics and films consisting of a SBT-BTN solid solution. The following three reasons can be given for the good ferroelectric properties in $(1-x)SBT-xBTN$ with $x=0.3-0.4$: (1) X-ray diffraction showed that stronger (115) and (200) lines appear in $x=0.3-0.4$ materials. This indicates that there is a better crystallization, which favors the larger polarization. (2) Larger grains are observed in materials with $x=0.3-0.4$.[2,3] (3) The stronger intensity of the Raman line at 813 cm^{-1} indicates that a large displacement of
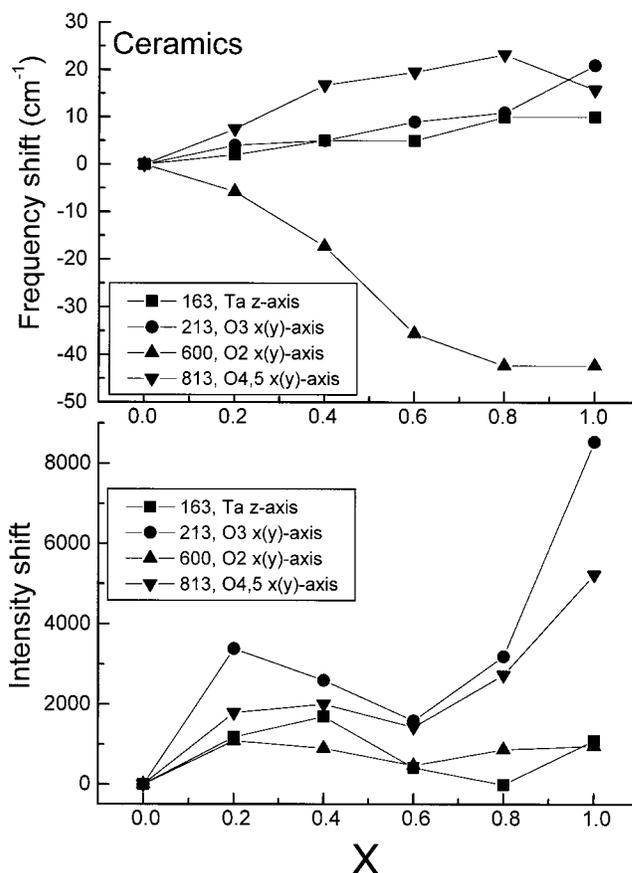

FIG. 3. Raman frequency and peak intensity as functions of x for the ceramics.

the Ta–O(4) or Ta–O(5) ions occurs with the addition of 30%–40% BTN, which is responsible for the increased spontaneous polarization.

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