

Lanthanum distribution and dielectric properties of intergrowth $\text{Bi}_{5-x}\text{La}_x\text{TiNbWO}_{15}$ ferroelectrics

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$\text{Bi}_{5-x}\text{La}_x\text{TiNbWO}_{15}$ ($x=0-1.50$) ceramics prepared by conventional solid-state reaction were studied using x-ray diffraction (XRD), dielectric spectroscopy and Raman scattering techniques. The XRD analysis implied that single-phase intergrowth bismuth layered perovskite structure was obtained for all the samples and when $x=0.75$, the Bi^{3+} in $(\text{Bi}_2\text{O}_2)^{2+}$ layer begins to be substituted by La^{3+} . The dielectric spectra showed that, when Bi^{3+} in $(\text{Bi}_2\text{O}_2)^{2+}$ is substituted, the Curie temperature becomes diffusive and the dielectric permittivity at room temperature is increased in a wide frequency range. Especially when $x=1.50$, the dielectric permittivity reaches its maximum of 270, nearly two times larger than that of the La^{3+} undoped sample. The Raman scattering experiments evidenced further that Bi^{3+} in $(\text{Bi}_2\text{O}_2)^{2+}$ is substituted when $x \geq 0.75$ and revealed the orthorhombic distortion of the octahedra is responsible for the increase of the dielectric permittivity at $x \geq 1.25$. © 2005 American Institute of Physics. [DOI: 10.1063/1.2132077]

The intergrowth bismuth layer-structured ferroelectrics (IBLSFs) have attracted considerable attention due to their interesting crystal structures and potential applications in information technology.¹⁻⁴ However, they also suffer from relatively low dielectric and ferroelectric properties, and there is still not enough work reported on improving these properties. In this letter, we report our recent studies on the influences of La^{3+} doping on the dielectric properties of an IBLSF $\text{Bi}_5\text{TiNbWO}_{15}$.¹ This study offers useful guidelines for designing ferroelectric and dielectric ceramics in a controllable manner.

The wafer specimens of $\text{Bi}_{5-x}\text{La}_x\text{TiNbWO}_{15}$ ($x=0.00, 0.25, 0.50, 0.75, 1.00, 1.25, 1.50$) with a diameter of 13 mm and a thickness of 1 mm were prepared by conventional solid-state reaction method. Appropriate amounts of high purity raw materials (in which excess Bi_2O_3 of 2 mol % out of the stoichiometry was added to compensate for the volatilization of bismuth during sintering at high temperatures) were first mixed and pre-sintered at 1173 K for 7 h then pressed into pellets and sintered at 1313–1373 K in air for 2 h. For x-ray diffraction (XRD) analysis, the sintered samples were crushed to fine powders and recorded using $\text{Cu K}\alpha$ radiation in a Rigaku D/max-2550V diffractometer. The dielectric spectra were performed on Pt-pasted samples by a HP4194A impedance analyzer in air at a heating rate of 3 °C/min. FT-Raman spectra were recorded on a Nicolet Nexus 950 bench equipped with a Raman module, a 1064 nm Nd:YVO₄ excitation laser, and a Ge detector. The spectra were measured at room temperature in the range of 3700–100 cm^{-1} with a resolution of 1 cm^{-1} .

The structure of $\text{Bi}_5\text{TiNbWO}_{15}$ is built up by a regular intergrowth of one half the unit cell of Bi_2WO_6 and one half the unit cell of $\text{Bi}_3\text{TiNbO}_9$, with the space group $\text{Pmc}2_1$ and

lattice constants a , b and c equal 2.0886(8), 0.5429(5), and 0.5406(4) nm, respectively.⁵ Figure 1 shows the XRD patterns of $\text{Bi}_{5-x}\text{La}_x\text{TiNbWO}_{15}$ powders. The coincidence of diffraction peaks for the samples at various x values indicates that La^{3+} doping does not affect the crystal structure. The inset in Fig. 1 shows the refined lattice constants estimated by the Rietveld method. With increasing La^{3+} doping content, there are two relatively apparent transitions that occurred at $x=0.50$ and $x=1.25$. It is widely accepted that, $(\text{Bi}_2\text{O}_2)^{2+}$ is a rigid layer and when substituting La^{3+} for Bi^{3+} , La^{3+} will preferentially enter A sites in perovskite-like layers.⁶ However, for the compounds $\text{Bi}_{5-x}\text{La}_x\text{TiNbWO}_{15}$, when $x > 1.00$ the La^{3+} will definitely enter into $(\text{Bi}_2\text{O}_2)^{2+}$ layers. So the lattice constants transition at $x=0.50$ implies the position variations for the substituting La^{3+} , i.e., when $x \geq 0.75$, the Bi^{3+} in $(\text{Bi}_2\text{O}_2)^{2+}$ begins to be substituted. This suggestion is supported by the dielectric spectroscopy and

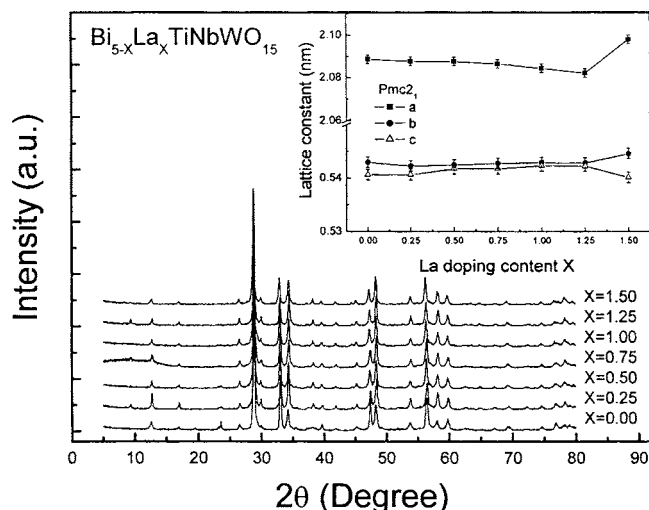


FIG. 1. X-ray diffraction patterns of $\text{Bi}_{5-x}\text{La}_x\text{TiNbWO}_{15}$ powders ($x=0.00-1.50$) at room temperature. Inset is the variation of lattice constants as a function of La doping content x .

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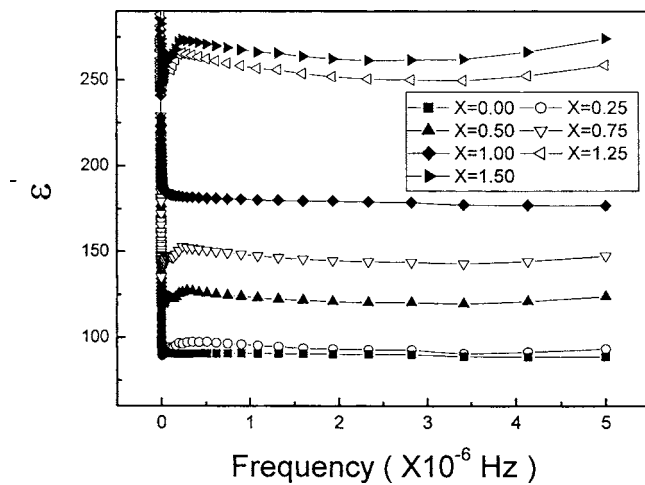


FIG. 2. The dielectric permittivity of $\text{Bi}_{5-x}\text{La}_x\text{TiNbWO}_{15}$ ceramics as a function of frequency, measured at room temperature.

Raman spectrum experiments. While the lattice constants transition at $x=1.25$ reveals too much La^{3+} substitution in the rigid $(\text{Bi}_2\text{O}_2)^{2+}$ layers the layers will deteriorate the bismuth layered perovskite structure. In fact, a secondary phase was observed when La^{3+} content is above 1.50.

Figure 2 shows the dielectric permittivity of IBLSFs $\text{Bi}_{5-x}\text{La}_x\text{TiNbWO}_{15}$ as a function of frequency from 100 Hz to 5 MHz at room temperature. It can be seen that the dielectric permittivity is almost constant in a wide range of frequencies. Furthermore, with increasing La^{3+} doping content, the dielectric permittivity is increased, especially at $x \geq 1.25$. When La^{3+} doping content $x=1.50$ the dielectric permittivity reaches a maximum of 260–270, nearly two times larger than that of the undoped sample. Correspondingly, the dielectric loss increases with increasing La^{3+} content. However, the dielectric loss is lower than 0.03, for all the samples at frequencies larger than 1 kHz. These results show definitely that the La^{3+} substituting for Bi^{3+} in $(\text{Bi}_2\text{O}_2)^{2+}$ layers can increase the dielectric permittivity of IBLSFs.

Figure 3 shows the temperature dependence of dielectric permittivity and dielectric loss for IBLSFs $\text{Bi}_{5-x}\text{La}_x\text{TiNbWO}_{15}$ at the frequency of 1 MHz. With increasing La^{3+} doping content, the phase transition temperature, T_c , shifts to a lower temperature range and, when $x \geq 0.75$ the phase transition peak becomes broad and diffu-

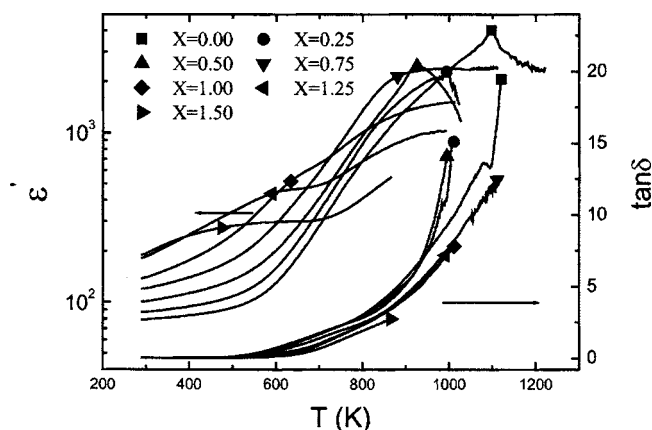


FIG. 3. The dielectric permittivity and dielectric loss of $\text{Bi}_{5-x}\text{La}_x\text{TiNbWO}_{15}$ ceramics as a function of temperature, measured at 1 MHz.

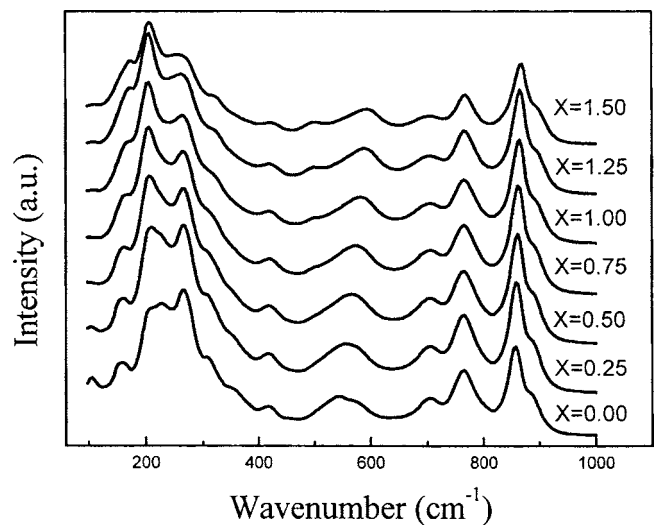


FIG. 4. The Raman spectra of $\text{Bi}_{5-x}\text{La}_x\text{TiNbWO}_{15}$ ceramics measured at room temperature.

sive. The decrease of T_c is due to the substitution of La^{3+} for Bi^{3+} , as the $6s^2$ lone pair electrons of Bi^{3+} have great influence on the Curie temperature.⁷ The diffusive character of phase transition peak occurring at $x \geq 0.75$ implies there is site disorder in $\text{Bi}_{5-x}\text{La}_x\text{TiNbWO}_{15}$ ceramics ($x=0.75, 1.00, 1.25, 1.50$). It is apparent from the relative b/c cell dimensions reported for Bi_2WO_6 (0.5458, 0.5437 nm),⁸ $\text{Bi}_3\text{TiNbO}_9$ (0.5440, 0.5394 nm),⁹ and $\text{Bi}_5\text{TiNbWO}_{15}$ (0.5429, 0.5406 nm)⁵ that the perovskite-like layer $[\text{WO}_4]$ is under compressive stress compared to the perovskite-like layers $[\text{BiTiNbO}_7]$. Furthermore, the stress is aggravated by A sites substitution. The sites disorder occurring at $x \geq 0.75$ helps relaxing the lattice mismatch and is consistent with the viewpoint mentioned above that Bi^{3+} in $(\text{Bi}_2\text{O}_2)^{2+}$ layers begins to be substituted at $x=0.75$. Additionally, from Fig. 3 it can be observed that the dielectric loss increases rapidly with increasing temperature. Fortunately, substituting La^{3+} for Bi^{3+} in $(\text{Bi}_2\text{O}_2)^{2+}$ can reduce dramatically the dielectric loss at high temperatures.

From Fig. 3 we know the monotonous increase of dielectric permittivity at room temperature is apparently related to the decrease and diffusivity of the Curie point. To further probe this problem from the viewpoint of phonon vibrations, Fig. 4 shows the Raman spectra and Fig. 5 shows the frequency shift of Raman modes of IBLSFs $\text{Bi}_{5-x}\text{La}_x\text{TiNbWO}_{15}$ at room temperature. At $x=0.00$, Raman bands around 157, 206, 228, 267, 418, 546, 704, 765, and 858 cm^{-1} are observed in the ceramic samples. With increasing La^{3+} doping content, the position and width of the bands are affected distinctly. According to previous studies,^{10,11} the bands can be assigned as follows: the 157 cm^{-1} band is associated with the vibration of the Bi^{3+} ions at A sites in the perovskite-like layers along the z direction (TO mode A_{1g}). The bands between 200 and 270 cm^{-1} represent the rocking mode of the octahedra (E_g character). The bands between 400 and 600 cm^{-1} can be assigned to the opposing excursions of the external apical oxygen atoms of the octahedra (E_g mode). When La^{3+} doping content $x \geq 0.75$, a new mode emerged at $\sim 550 \text{ cm}^{-1}$ which is consistent with orthorhombic distortion, generating $E_g \rightarrow B_{2g} + B_{3g}$ splitting. The bands at 765 and 858 cm^{-1} represent the symmetric stretching of the WO_6 and $(\text{Ti},\text{Nb})\text{O}_6$ octahedra, respectively. Whereas the band

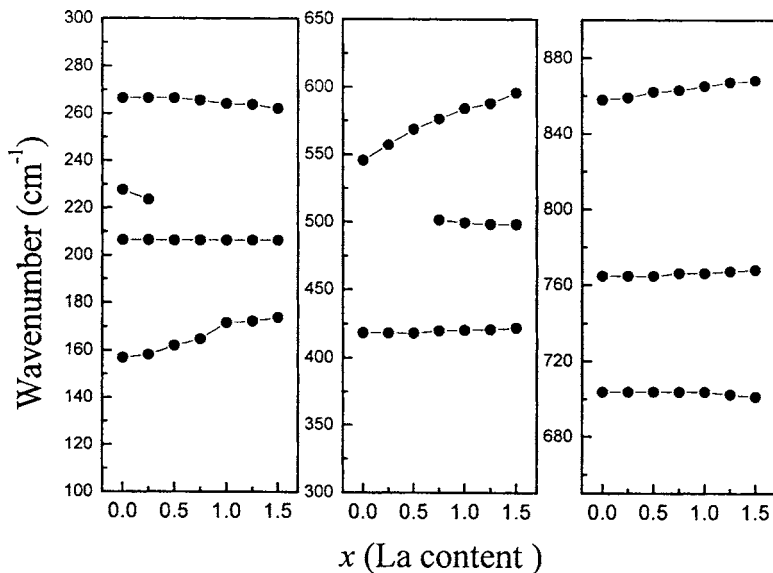


FIG. 5. The frequency shift of Raman modes of $\text{Bi}_{5-x}\text{La}_x\text{TiNbWO}_{15}$ ceramics.

704 cm^{-1} and the right shoulder of the band 858 cm^{-1} are also due to the orthorhombic distortion of the octahedra.

Since Raman scattering is sensitive to the variations of local structures, the Raman shift with different La^{3+} content, as shown in Fig. 5, gives us valuable information about atomic or ionic substitution and polarization. For example, when Bi^{3+} at A sites is substituted by lighter La^{3+} ions, the corresponding vibration mode (157 cm^{-1} at $x=0.00$) shifts quickly to higher frequencies. However, when $x \geq 1.00$ (the maximum substitution of Bi^{3+} at A site), the mode at $\sim 160\text{ cm}^{-1}$ increases little. From the Raman shift corresponding to the vibrations of WO_6 and $(\text{Ti,Nb})\text{O}_6$ octahedra we can see that the substitution of Bi^{3+} at $(\text{Bi}_2\text{O}_2)^{2+}$ layers take place when $x \geq 0.75$. When $x \leq 0.50$, there is just Bi^{3+} at A sites substituted, thus the wave number corresponding to the vibration of $(\text{Ti,Nb})\text{O}_6$ octahedra ($\sim 858\text{ cm}^{-1}$) increases quickly, whereas the vibration mode corresponding to WO_6 octahedra ($\sim 765\text{ cm}^{-1}$) is not influenced and the corresponding wave number does not change. Nevertheless, when $x \geq 0.75$, the Bi^{3+} at $(\text{Bi}_2\text{O}_2)^{2+}$ layer is substituted, then the wave number corresponding to the vibration of WO_6 octahedra increases and the Raman shift corresponding to the vibration of $(\text{Ti,Nb})\text{O}_6$ octahedra relaxes. Based on the aforementioned analysis, we can further attribute the bands 267 and 418 cm^{-1} to the vibrations related to WO_6 octahedra and attribute the bands 206 , 228 and 546 cm^{-1} to the vibrations related to $(\text{Ti,Nb})\text{O}_6$ octahedra.

It should be noted that stress can also induce Raman shift. Is the Raman shift corresponding to the vibrations of WO_6 and $(\text{Ti,Nb})\text{O}_6$ octahedra due to the stress within the compounds $\text{Bi}_{5-x}\text{La}_x\text{TiNbWO}_{15}$? For the IBLSF $\text{Bi}_5\text{TiNbWO}_{15}$, in view of the perovskite-like layer $[\text{WO}_4]$ suffers compressive stress and A sites substitution aggravates the stress, as mentioned above. If the Raman shift reflected the stress within $\text{Bi}_{5-x}\text{La}_x\text{TiNbWO}_{15}$, the mode corresponding to the vibrations of WO_6 , i.e., the band at 765 cm^{-1} , should shift with A sites substitution. However, we did not

observe this phenomenon. As a result, we attribute the Raman shift to the variations of local structures induced by La^{3+} substitution.

The variation of wave number at $\sim 706\text{ cm}^{-1}$ for samples with different La^{3+} content implies that, when $x \geq 1.25$, the substituted content of Bi^{3+} in $(\text{Bi}_2\text{O}_2)^{2+}$ layers is high enough to aggravate the orthorhombic distortion of the octahedra and the remarkable increase of dielectric permittivity may be due to it.

In summary, lanthanum distribution and dielectric properties of $\text{Bi}_{5-x}\text{La}_x\text{TiNbWO}_{15}$ ceramics were studied by XRD, dielectric spectroscopy and Raman scattering techniques. It was found that, Bi^{3+} in $(\text{Bi}_2\text{O}_2)^{2+}$ is substituted by La^{3+} when $x \geq 0.75$, and the appreciable increase of dielectric permittivity at room temperature implies the compounds are promising candidates as materials in some dielectric applications.

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