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W doping-dependent structural and ferroelectric properties of $SrBi_2Nb_2O_9$ ferroelectric ceramics

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Abstract

The structural and ferroelectric characteristics of $SrBi_2(Nb_{1-x}W_x)_2O_9$ ($x = 0$–0.12) ferroelectric ceramics were investigated. $SrBi_2(Nb_{1-x}W_x)_2O_9$ ceramics consisted of a single-phase layered perovskite structure when x was less than 0.06. Uniform microstructure and grain size reduction were observed after the introduction of W. The maximum remanent polarization of $16\,\mu C/cm^2$ appeared at $x = 0.03$, and the coercive field decreased with increasing concentration of W. The ferroelectric behavior of $SrBi_2(Nb_{1-x}W_x)_2O_9$ ceramics is interpreted based on the Raman measurement.

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Keywords: Ferroelectricity; Niobates; Raman spectra

1. Introduction

As a potential candidate for non-volatile random access memory (NVRAM) devices, $SrBi_2Nb_2O_9$ (SBN) ferroelectric material belonging to the Aurivillius family has received great attention for its high Curie temperature, low leakage current, excellent fatigue resistance and excellent retention property [1]. The Aurivillius family with the bismuth-layered perovskite-type structure can be described by the general formula $(Bi_2O_2)^{2+}(A_{m-1}B_mO_{3m+1})^{2-}$, where A sites can accommodate Sr^{2+}, Ca^{2+}, Bi^{3+} or Pb^{2+}, etc., B sites can be taken by Ta^{5+}, Nb^{5+}, Ti^{4+}, etc., and n refers to the number of the corner-sharing octahedra to form perovskite slabs [1,2]. Thus, there is a possibility of the cations doping modified ferroelectric properties for the Aurivillius family. And great efforts have been carried out to investigate the doping effects on the ferroelectric properties of the bismuth-containing layered perovskite-type material. Noguchi and Miyayama [3] reported an improved remanent polarization ($2P_r$) in $Bi_4Ti_3O_{12}$ after the incorporation of slight higher-valent cations like V^{5+} into B sites. Shrivastava et al. [4] found that the incorporation of La cations into A sites up to 50% continuously decreased the Curie temperature in SBN ferroelectric ceramics . Das et al. [5] reported the improved remanent polarization of SBN and $SrBi_2Ta_2O_9$ (SBT) thin films, when a small amount of Ca cations were incorporated into A sites. Gu et al. [6] found that $BiFeO_3$ doping up to 20% in SBN ceramics improved the Curie temperature and decreased the sintering temperature. Several research groups [7] reported that the incorporation of V cation into B sites in SBN ceramics led to a higher Curie temperature. The substitution of W cations for Ti cations in B sites in SBT ceramics induced a higher Curie temperature and lower dielectric loss [8]. Wang et al. [9] reported enhanced dielectric properties in SBN/Ag composites. Meanwhile, many interesting physical properties have been found in modified perovskite oxides [10]. However, there are few reports on the W doping effects on the ferroelectric properties of SBN material. In this work, we investigated the ferroelectric properties and structural modifications of the SBN ceramics with various concentrations of W, and found the coercive field of the

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SBN ceramics decreased with increasing concentration of W. The ferroelectric behavior of $SrBi_2(Nb_{1-x}W_x)_2O_9$ ceramics is interpreted based on the Raman measurement.

2. Experimental

The W doped $SrBi_2(Nb_{1-x}W_x)_2O_9$ ($x = 0.0$, 0.03, 0.06, 0.12) ferroelectric ceramic samples were prepared by the solid-state reaction method. The reactive powders ($SrCO_3$, Bi_2O_3, Nb_2O_5 and WO_3) were weighed in a desired molar ratio with approximately 3 mol% excess Bi_2O_3 to compensate for the loss of Bi_2O_3 at a high sintering temperature. The powders were mixed by ball milling for 2 h, and then calcined in a crucible at 860 °C for 2 h. The calcined mixture was ball-milled again, and pressed into pellets. The pellets were sintered in a covered crucible at 1040 °C for 2 h to produce samples with the diameter of 1 mm. The phase formation and crystalline quality of sintered samples were identified by an X-ray diffractometer with Cu Kα radiation. Several sintered samples with various W concentrations were broken, and heated at 900 °C for 30 min, then quickly cooled down to room temperature in air. The recrystallized cross-section microstructure of sintered samples was observed by scanning electron microscopy (SEM). The ferroelectric hysteresis loops of thinned and silver-electroded samples with thickness of 0.3 mm were measured using a RT6000 ferroelectric tester. Raman spectra of sintered samples excited by 532 nm radiation were measured in backscattering geometry (JY-HR800).

3. Results and discussions

The X-ray diffraction spectra of the four compositions of $SrBi_2(Nb_{1-x}W_x)_2O_9$ ceramics ($x = 0.0$, 0.03, 0.06, 0.12) are shown in Fig. 1. A single phase of the layered perovskite structure can be kept when the W concentration is up to 0.03. Unidentified extra peaks (labeled by *) are detected in the $SrBi_2(Nb_{1-x}W_x)_2O_9$ samples with the W concentration of 0.06 and 0.12. A similar result was also found in W-doped SBT ceramics [8], which indicates that W, compared with V [11], is not easy to be incorporated into the crystal lattice of SBN, mainly because the valence of W ion is higher than that of Nb ion. The substitution of W^{6+} for Nb^{5+} in SBN would induce A-site cation vacancies in perovskite layers, which leads to an increase of internal stress for the shrinkage of unit cell volume [8]. High concentration of W ions in the crystal lattice of SBN will result in strong stress, which will expel other W ions from the crystal lattice of SBN.

Fig. 2(a), (b) is the cross-section SEM micrographs of $SrBi_2(Nb_{1-x}W_x)_2O_9$ ($x = 0$, 0.06) ceramics. The undoped SBN ceramics were composed of the plate-shaped grains (shown in Fig. 2(a)). With increasing W concentration, the plate-shaped grains became granular-shaped grains (Fig. 2(b)), which indicates that W-doping in SBN ceramics effectively restrains crystallite growth in preferential orientation and results in a uniform microstructure.

Fig. 3 shows the ferroelectric hysteresis loops for the $SrBi_2(Nb_{1-x}W_x)_2O_9$ samples under an applied electric field of 100 kV/cm. The coercive field (E_c) of $SrBi_2(Nb_{1-x}W_x)_2O_9$ ceramics decreases from 73.5 kV/cm ($x = 0$) to about 57 kV/cm ($x = 0.12$), which indicates that the W-doping in SBN ferroelectric ceramics can decrease the

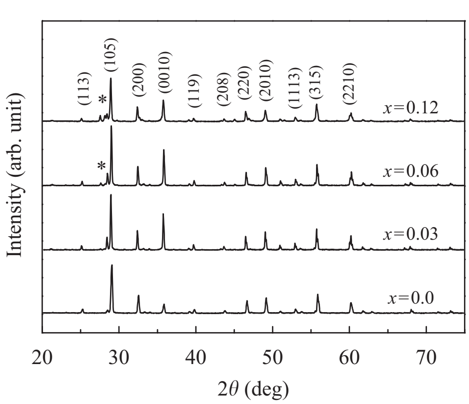

Fig. 1. X-ray diffraction patterns of $SrBi_2(Nb_{1-x}W_x)_2O_9$ ($x = 0.0$, 0.03, 0.06, 0.12) ferroelectric ceramic samples.

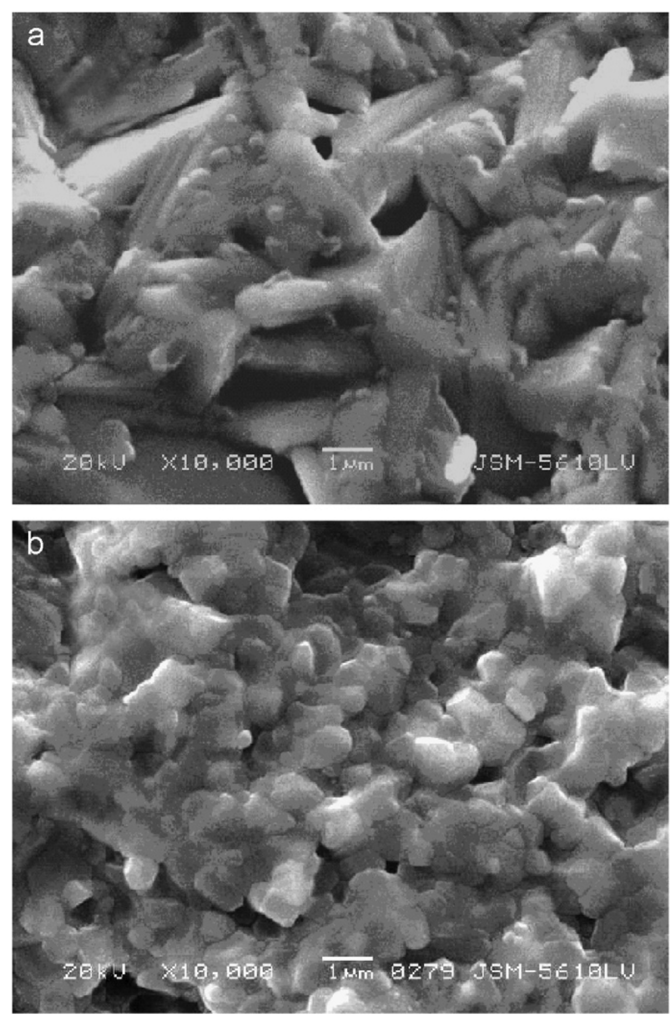

Fig. 2. SEM fracture micrographs of $SrBi_2(Nb_{1-x}W_x)_2O_9$ ferroelectric ceramic samples with different W concentrations (a) $x = 0$, (b) $x = 0.06$.

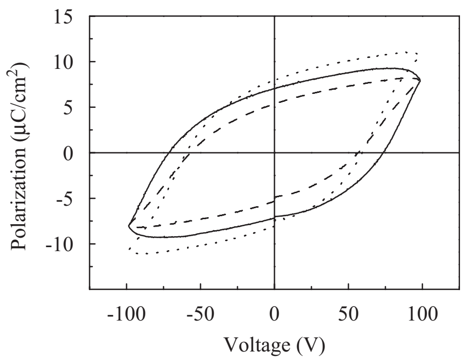

Fig. 3. Hysteresis loops of $SrBi_2(Nb_{1-x}W_x)_2O_9$ ferroelectric ceramic samples under a applied electric field of 100 kV/cm at room temperature. The hysteresis loops for $x = 0.0$,0.03, 0.12 is presented by the solid, dotted and dashed curves, respectively.

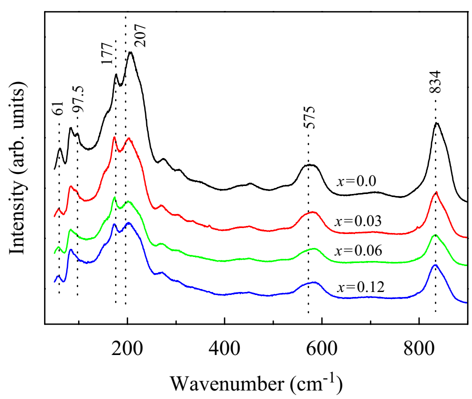

Fig. 4. Room temperature Raman spectra of $SrBi_2(Nb_{1-x}W_x)_2O_9$ ferroelectric ceramic samples.

coercive field. The $SrBi_2(Nb_{1-x}W_x)_2O_9$ ceramics present a maximum remanent polarization ($2P_r$) of about 16 μC/cm at $x = 0.03$, which means that a small amount of W doping in SBN ceramics can increase the remanent polarization.

The Raman spectra of $SrBi_2(Nb_{1-x}W_x)_2O_9$ ceramics were measured at room temperature to identify the influence of W on the lattice vibrational mode of SBN ceramics (shown in Fig. 4). The 834 cm^{-1} mode assigned to the NbO_6 octahedral stretching mode becomes more symmetric with W substitution, which should be due to the increased "rattling space" deriving from smaller W^{6+} cations substitution for larger Nb^{5+} cations [8,12]. The increased "rattling space" could be correlated with the increasing remanent polarization of $SrBi_2(Nb_{1-x}W_x)_2O_9$ ($x = 0$–0.03) [8]. With the increase in W concentration, the blue shift of the 575 cm^{-1} mode corresponding to a rigid sublattice mode indicates that the equal and opposite displacements of positive and negative ions are slightly changed [12], which lower the activation barrier required for the domain motion, and then lead to a decrease in E_c. The enhancement of the peak at the 177 cm^{-1} which originates from Nb vibration in a–b plate proves the existence of the increased "rattling space" [12]. The wave numbers at 61 and 97.5 cm^{-1} for $SrBi_2(Nb_{1-x}W_x)_2O_9$ ceramics correspond to the low optical phonon modes. The weak or strong behavior of their corresponding peaks might result from the effects of W incorporations into NbO_6 octahedra on the chemical bonds in Bi_2O_2 layers and the Sr^{2+} ions in A-site [5,12].

4. Conclusions

In summary, SBN ceramics with various W contents were prepared by the solid-state reaction method. W doping effectively restrains crystallite growth in preferential orientation and results in a uniform microstructure in SBN ceramics. Meanwhile W-doping decreases the coercive field from 73.5 kV/cm for undoped SBN ceramics down to 57 kV/cm for SBN ceramics with 12% W concentration. When the W concentration is less than 6%, SBN ceramics consist of a single phase, and exhibit good ferroelectric properties. Raman spectra of W-doped SBN ceramics exhibited a strong dependence on W concentration, which reveals one reason for the enhanced ferroelectric behavior of SBN ceramics.

Acknowledgments

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