W doping-dependent structural and ferroelectric properties of SrBi$_2$Nb$_2$O$_9$ ferroelectric ceramics

Jie Qiu$^a$, Guo-Zhen Liu$^a$, Meng He$^{a,*}$, Hao-Shuang Gu$^b$, Tao-Sheng Zhou$^b$

$^a$Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China
$^b$Faculty of Physics and Electronic Technology, Hubei University, Wuhan 430062, China

Received 13 June 2007; received in revised form 26 June 2007; accepted 27 June 2007

Abstract

The structural and ferroelectric characteristics of SrBi$_2$(Nb$_{1-x}$W$_x$)$_2$O$_9$ ($x = 0–0.12$) ferroelectric ceramics were investigated. SrBi$_2$(Nb$_{1-x}$W$_x$)$_2$O$_9$ 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 $\text{mC/cm}^2$ 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$_x$)$_2$O$_9$ ceramics is interpreted based on the Raman measurement.

Keywords: Ferroelectricity; Niobates; Raman spectra

1. Introduction

As a potential candidate for non-volatile random access memory (NVRAM) devices, SrBi$_2$Nb$_2$O$_9$ (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$_2$O$_2$)$^{2+}$($A_{n-1}B_nO_{3n+1}$)$^{2+}$, 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. 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 (2$P_r$) in Bi$_4$Ti$_3$O$_{12}$ 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$_2$Ta$_2$O$_9$ (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
SBN ceramics decreased with increasing concentration of W. The ferroelectric behavior of SrBi$_2$(Nb$_{1-x}$W$_x$)$_2$O$_9$ ceramics is interpreted based on the Raman measurement.

2. Experimental

The W doped SrBi$_2$(Nb$_{1-x}$W$_x$)$_2$O$_9$ (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$_2$O$_3$, Nb$_2$O$_5$ and WO$_3$) were weighed in a desired molar ratio with approximately 3 mol% excess Bi$_2$O$_3$ to compensate for the loss of Bi$_2$O$_3$ 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$_x$)$_2$O$_9$ 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$_x$)$_2$O$_9$ 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$_x$)$_2$O$_9$ (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$_x$)$_2$O$_9$ samples under an applied electric field of 100 kV/cm. The coercive field ($E_c$) of SrBi$_2$(Nb$_{1-x}$W$_x$)$_2$O$_9$ 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. 3. Hysteresis loops of SrBi$_2$(Nb$_{1-x}$W$_x$)$_2$O$_9$ ferroelectric ceramic samples under an applied electric field of 100 kV/cm at room temperature. The hysteresis loops for $x = 0, 0.03, 0.12$ is presented by the solid, dotted and dashed curves, respectively.

Fig. 4. Room temperature Raman spectra of SrBi$_2$(Nb$_{1-x}$W$_x$)$_2$O$_9$ ferroelectric ceramic samples.

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$_2$O$_2$ 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

This work was supported by National Natural Science Foundation of China and National Basic Research Program of China.

References