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Bismuth layered ceramic solid solution with high temperature piezoelectricity endurance and low sintering temperature☆

Cai Kai[a,**], Pingye Deng[a], Yunli Wang[c], Dong Guo[b,c,*]

[a] Beijing Center for Physical and Chemical Analysis, Beijing 100089, China
[b] School of Materials Science & Engineering, Beihang University, Beijing 100191, China
[c] Institute of Acoustics, Chinese Academy of Sciences, Beijing 100190, China

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ABSTRACT

In this study, we report the electrical performance and structure of Li and Mn codoped Aurivillius type solid solution ceramics with a composition $(CaBi)_{1-x}(LiMn)_xBi_6NbTi_5O_{24}$ (x = 0–0.04) sintered under different temperatures. The results indicate that single phase structure with a lattice similar to that of the end member $CaBi_4Ti_4O_{15}$ could be formed in a wide sintering temperature range for all the compositions investigated. All composite samples show piezoelectric constant values about 2–3 times of that of the designed constituent phase $CaBi_4Ti_4O_{15}$ and Bi_3TiNbO_9. Interestingly, the samples sintered under a relatively low temperature around 960 °C showed the highest d_{33} and best temperature stability of piezoelectricity. This was attributed to a suppressed Bi evaporation. The results indicated that formation of compound or solid solution system was an effective way in improving the piezoelectric performance. Although a relatively lower Curie temperature (T_c) compared to that of the single phase end member was obtained in the compound system, all the samples still showed a depolarization temperature higher than 500 °C, while the temperature stability below T_c seems to be an issue deserving further investigation.

1. Introduction

Piezoelectric ceramics are widely used in sensing, actuation, and energy harvesting, etc. The rapid development of piezoelectric devices for automotive and aerospace industries has put increasing demand on piezoelectric materials capable of working at elevated temperatures. Compared to the conventional Pb(Zr,Ti)O3 (PZT), the perovskite Bi-based high temperature ceramics and the tungsten bronze type lead metaniobate have a relatively high Curie temperature of about 460 °C and 530 °C, respectively [1–3]. Recently, even higher T_c was achieved in Bi-based perovskite ceramics [4,5]. For some special cases like sensors for material processing and chemical engineering, an operation temperature of 400 °C or even higher may be required. In such cases, bismuth layer-structured ferroelectrics (BLSFs) or Aurivillius-type ceramics seem to be the only available materials because of their ultra-high Curie temperature (Tc) in the range of about 600 °C to 900 °C [6,7]. The general formula of BLSFs is $(Bi_2O_2)^{2+}(A_{m-1}B_mO_{3m+1})^{2-}$, which consist of regular $(A_{m-1}B_mO_{3m+1})^{2-}$perovskite-like slabs separated by $(Bi_2O_2)^{2+}$ layers along the crystallographic c-axis. In addition to the ultrahigh T_c, BLSFs also have small dielectric constants (ε_r), low aging rates, and merits of low cost and non-toxicity, etc. [6,7]. However, because the spontaneous polarization and the mass transport during sintering are restricted in the layered structure, practical application of BLSFs are seriously limited by their very low piezoelectricity and the difficulty in fabricating dense ceramics. Special techniques like hot pressing have been widely used [8,9], however, this method usually leads to anisotropic performance, poor mechanical properties and high cost.

Composition adjustment or fabrication of solid solution (compound) are effective approaches to modify the sintering activity, microstructure and electrical properties of piezoelectric ceramics. Similar modification effects were also reported in BLSFs. Concerning composite systems, $CaBi_2Nb_2O_9$-$BaBi_2Nb_2O_9$ [10] and $SrBi_2Nb_2O_9$-Bi_3TiNbO_9, [11] etc., with largely enhanced piezoelectricity than those of the end members have been reported. Nevertheless, BLSF solid solution systems, particularly those doped systems, are much less investigated as compared to the studies in traditional piezoelectric ceramics. $CaBi_4Ti_4O_{15}$ (CBT) and Bi_3TiNbO_9 (BTN) are two typical BLSF family materials with a high T_c of about 790 °C and 940 °C respectively, however, they

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* Corresponding author at: School of Materials Science & Engineering, Beihang University, Beijing 100083, China.

** Corresponding author.

E-mail addresses: caikai@tsinghua.org.cn (K. Cai), dong.guo@buaa.edu.cn (D. Guo).

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have a low piezoelectric coefficient (d_{33}) of only about 7 pC/N [12,13] and 4 pC/N, [14,15] respectively. To improve the piezoelectric activity and to understand the effect of solid solution formation on the structure and performance of BLSF ceramics, in this study lithium and manganese codoped solid solution ceramics $(CaBi)_{1-x}(LiMn)_xBi_6NbTi_5O_{24}$ were investigated.

2. Experimental

The solid solution BLSF ceramics with the composition $(CaBi)_{1-x}(LiMn)_xBi_6NbTi_5O_{24}$ (hereafter referred to as CBNT-xLiMn) with different codoping mole fraction (x = 0–0.04) were prepared by the conventional solid state reaction method. Analytically pure $CaCO_3$, Bi_2O_3, Li_2CO_3, $MnCO_3$, Nb_2O_5 (Beijing Chemical Reagent Corp.) and commercial grade TiO_2 (Shandong Hengze Corp.) powders were used as the raw materials, which were mixed in stoichiometric ratio (with 1 wt% excess amounts of Bi_2O_3) and ball-milled, dried, grinded, and calcined at 800 °C for 150 min. Then the powders were pressed into pellets with a diameter of ~10 mm and a thickness of ~ 1 mm mixed with polyvinyl alcohol (PVA) binder and sintered at different temperatures from 930 °C to 1080 °C for 2.5 h to give the ceramic samples. X-ray diffraction (XRD) profiles were recorded by a Bruker D8 Advance diffractometor with Cu Kα1 radiation. The lattice parameters were calculated from the interplanar distance derived from the XRD patterns by refinement with Pearson-VII function. Then the relative densities were derived from the lattice parameters and the densities measured by the Archimedes method. The sample morphology was observed by scanning electron microscopy (SEM) with a Hitachi S-4800 instrument. The samples for electrical characterization were pasted with silver electrodes. The temperature dependence of relative dielectric constant εr was measured by a PC controlled programmable HP4294A impedance analyzer at 1 MHz. The d_{33} of the samples that have been poled at 180 °C for 20 min under a voltage of 6–7 kV were tested by a ZJ-3A quasi-static d_{33} meter (Institute of Acoustics, Chinese Academy of Sciences). The planar electromechanical coupling factor (k_p) were measured by the resonance and anti-resonance method. A HP4140 B pA Meter equipped with a HP16055A Test Fixture was used to measure the resistivity. The ferroelectric hysteresis loops were measured by a Precision LC ferroelectric testing system (Radiant Corp. USA). High temperature endurance of piezoelectricity was characterized by measuring the room temperature d_{33} of the samples that have been heated at various temperatures for 1 h.

3. Result and discussion

Fig. 1a shows the XRD patterns of CBNT-xLiMn samples with different Li and Mn content that have been sintered at 930 °C. This relatively low sintering temperature is used due to consideration to control Bi evaporation. Although compound samples have a designed composition with equal mole content of the two end members, they still show a main structure very close to that the $CaBi_4Ti_4O_{15}$ (PDF#52-1640) phase with very weak diffraction peaks corresponding to $Bi_3TiNbO9$ phase (PDF#39-0233) or other impurity phase, indicating that a Aurivillius type homogeneous solid solution with typical CBT based orthorhombic symmetry was obtained. In another word, the BTN end member seems to have been dissolved in the CBT main lattice. According to the XRD intensity change, a Li and Mn codoping level of 0.01 have the best effect in improving sintering and crystallization. Indeed, the CBNT-0.01LiMn sample has the highest d_{33} (see Table 2). The XRD patterns of the CBNT-0.01 samples that have been sintered at different temperatures are shown in Fig. 1b. The similar XRD patterns can be in a rather wide sintering temperature range indicate that the com-

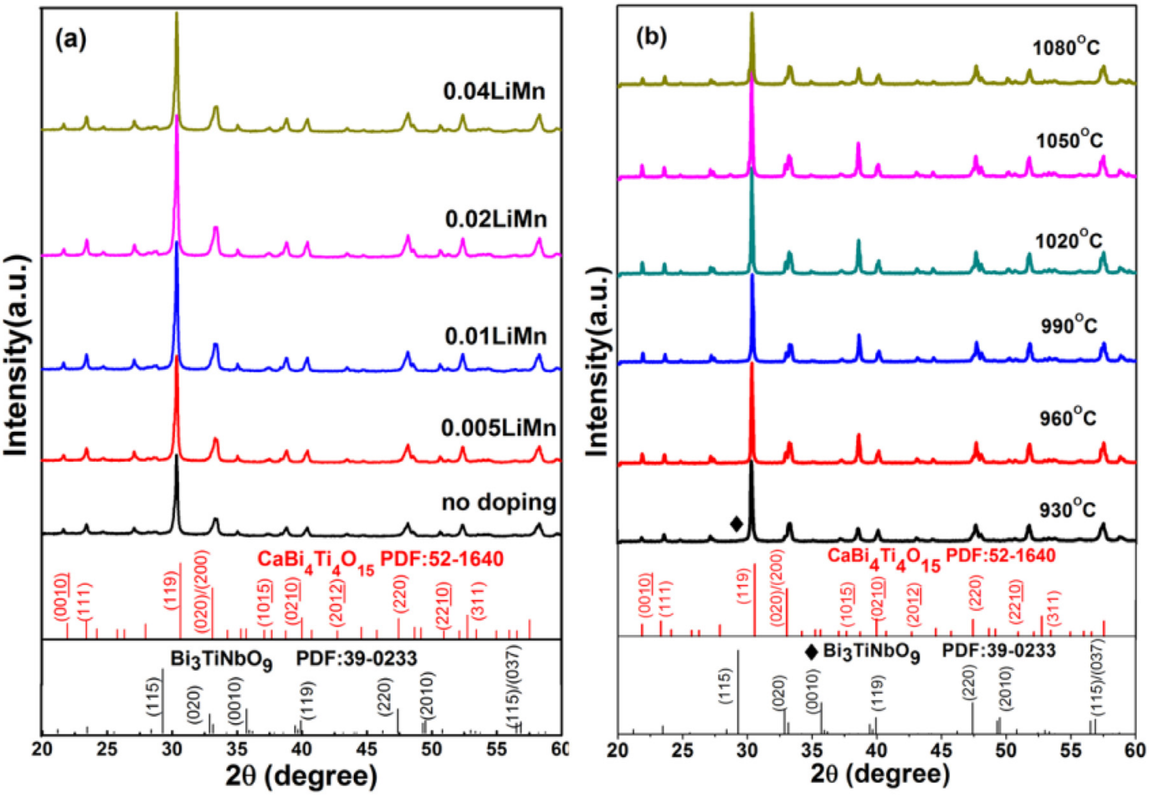

Fig. 1. (a) XRD patterns of CBNT-xLiMn samples with increasing codoping level (x = 0 − 0.4). (b) XRD patterns of the CBNT-0.01LiMn samples sintered under different temperatures. The reference PDF#52-1640 and #39-0233 patterns for CBT and BTN, respectively, are shown at the bottom for comparison.