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Phase formation, electrical properties and morphotropic phase boundary of $0.95Pb(Zr_xTi_{1-x})O_3$–$0.05Pb(Mn_{1/3}Nb_{2/3})O_3$ ceramics

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Abstract

Ferroelectric ceramics in specific composition of $0.95Pb(Zr_xTi_{1-x})O_3$–$0.05Pb(Mn_{1/3}Nb_{2/3})O_3$ or PZT–PMnN (with $x=0.46$, 0.48, 0.50, 0.52, and 0.54) have been investigated in order to identify the morphotropic phase boundary (MPB) composition. The effects of Zr/Ti ratio on phase formation, dielectric and ferroelectric properties of the specimens have also been investigated and discussed. X-ray diffraction patterns indicate that the MPB of the tetragonal and rhombohedral phase lies in $x=0.52$. The crystal structure of PZT–PMnN appeared to change gradually from tetragonal to rhombohedral phase with increasing Zr content. The dielectric and ferroelectric properties measurements also show a maximum value (ε_r, tan δ and P_r) at Zr/Ti=52/48, while the transition temperature decreases with increasing Zr content.

Keywords: C. Dielectric properties; C. Ferroelectric properties; MPB

1. Introduction

Nowadays, lead free piezoelectric ceramics, such as $BaTiO_3$ or BT [1–3], $(Bi_{1/2}K_{1/2})TiO_3$ or BKT [4], $(Bi_{1/2}K_{1/2})TiO_3$–$BaTiO_3$ or BKT–BT [5], $(K_{1/2}Na_{1/2})NbO_3$ or KNN [6,7], $(Bi_{1/2}Na_{1/2})TiO_3$ [BNT]-based ceramics [8,9] have been actively studied to replace PZT-based materials from the viewpoint of environmental protection. However, no materials recently replacing PZT has higher piezoelectricity especially at a composition near the morphotropic phase boundary (MPB) which has tetragonal and rhombohedral phases with the coexistence of 14 orientation states: 6-tetragonal and 8-rhombehedral [10]. This is essential to allow the strong polarization for piezoelectricity. This compound also possesses high spontaneous polarization and high Curie temperature ($T_c=390$ °C) [10]. PZT compositions belong to the classical piezoelectric materials which can be used for microelectromechanical systems (MEMS) applications because of their excellent electromechanical coupling coefficient, piezoelectric and pyroelectric properties. However, the disadvantages of PZT ceramics are their high loss due to their highly hysteretic characteristics and relatively high Curie temperature (T_c) [10]. Therefore, most commercial PZT ceramics are designed in the vicinity of the MPB with various doping methods in order to achieve high properties such as PZT–PMgN [11], PZT–PCN [12], PZT–PNN [13], and PZT–PZN [14].

$Pb(Zr_xTi_{1-x})O_3$–$Pb(Mn_{1/3}Nb_{2/3})O_3$ or PZT–PMnN ceramic system can be expected to have low heat generation in the large vibration velocity and high mechanical quality factor (Q_m) value. In view of such advantages, PZT–PMnN ceramics are used as an excellent candidate for the high power applications. Investigations on PZT–PMnN ceramic systems have already shown excellent electrical properties with the composition at 0.95 PZT–0.05 PMnN [15]. However, there have been no systematic studies on the relationship between Zr/Ti ratio, physical and electrical properties of ceramics within specific morphotropic phase boundary (MPB) compositions of PZT and PMN. Therefore, the overall purpose of this study is to determine the influence of Zr/Ti ratio on phase formation behavior, dielectric and ferroelectric properties of the $0.95Pb(Zr_xTi_{1-x})$

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O_3–$0.05Pb(Mn_{1/3}Nb_{2/3})O_3$ (where $x=0.46$, 0.48, 0.50, 0.52, and 0.54) ceramic system.

2. Experimental

The ceramics studied were fabricated according to the formula: $0.95Pb(Zr_xTi_{1-x})O_3$–$0.05Pb(Mn_{1/3}Nb_{2/3})O_3$, where $x=0.46$, 0.48, 0.50, 0.52, and 0.54. Raw materials of PbO, ZrO_2, TiO_2, MnO, and Nb_2O_5 with $>99\%$ purity were used to prepare samples. In the present work, the $0.95Pb(Zr_xTi_{1-x})O_3$–$0.05Pb(Mn_{1/3}Nb_{2/3})O_3$ samples were prepared using the conventional solid-state reaction of raw materials. The powders were mixed by a vibratory-milling technique in ethanol for 6 h. After drying, the product was calcined in an alumina crucible at a temperature of 950 °C for 2 h [12]. The calcined powders were uniaxially cold-pressed at 5000 psi into disc-shaped pellets with a diameter of 10 mm and a thickness of 1–2 mm, with 3 wt% poly (vinyl alcohol) (PVA) added as a binder. Following binder burnout at 500 °C, the pellets were sintered at 1200 °C for 2 h at a heating/cooling rate of 5 °C/min [12].

The phase structure of the powders was analyzed via X-ray diffraction (XRD; Bruker-AXS D8). The dielectric properties of the samples were measured using an automated measurement system. An Agilent 4284 A LCR meter was used to measure the dielectric properties over a wide temperature range using a NorECS ProboStat high temperature measurement cell. The room temperature ferroelectric properties were examined using a simple Sawyer–Tower circuit at fixed measuring frequency of 50 Hz.

3. Results and discussion

Effects of Zr/Ti ratios on phase formation of $0.95Pb(Zr_xTi_{1-x})O_3$–$0.05Pb(Mn_{1/3}Nb_{2/3})O_3$ ceramics have been investigated, where the XRD patterns for $x=0.46$, 0.48, 0.50, 0.52 and 0.54 are shown in Fig. 1. Phase formation of the specimens was characterized by XRD technique, showing a perovskite structure for all compositions. In the XRD patterns, the crystal structure of the specimens appears to change gradually from tetragonal (correlated with JCPDS File no. 50-0346) to rhombohedral (correlated with JCPDS File no. 73-2022) with increasing Zr content, as presented in Fig. 1(a). In addition, the c/a ratio calculation of the samples varies from 1.00 to 0.91 at $x=0.46$ to 0.54, respectively, confirming rhombohedral-rich phase with increasing Zr content (Table 1). As shown in Fig. 1(b), XRD peak profiles of the $(200)_T$ and $(002)_T$ peaks at $x=0.46$–0.50 indicate the tetragonal phase. At the $x=0.52$ composition, $(020)_R$ peak is observed with $(200)_T$ and $(002)_T$ peaks, indicating the coexistence of the tetragonal and rhombohedral phases. The $(020)_R$ peak in compositions $x=0.52$ and 0.54 have indicated that the crystal has transformed into a rhombohedral phase. There also appears coexistence between tetragonal and rhombohedral phases around Zr/Ti = 52/48, as shown in Fig. 1(b). Previously, a similar behavior was also observed with increasing Zr content in PZT [16], PZT–PZN [17], PZT–PCN [18] and PZT–SiO_2 [19] ceramics. To a first approximation, it could be stated that the composition with $x=0.52$ is close to the MPB of the 0.95PZT − 0.05PMnN system.

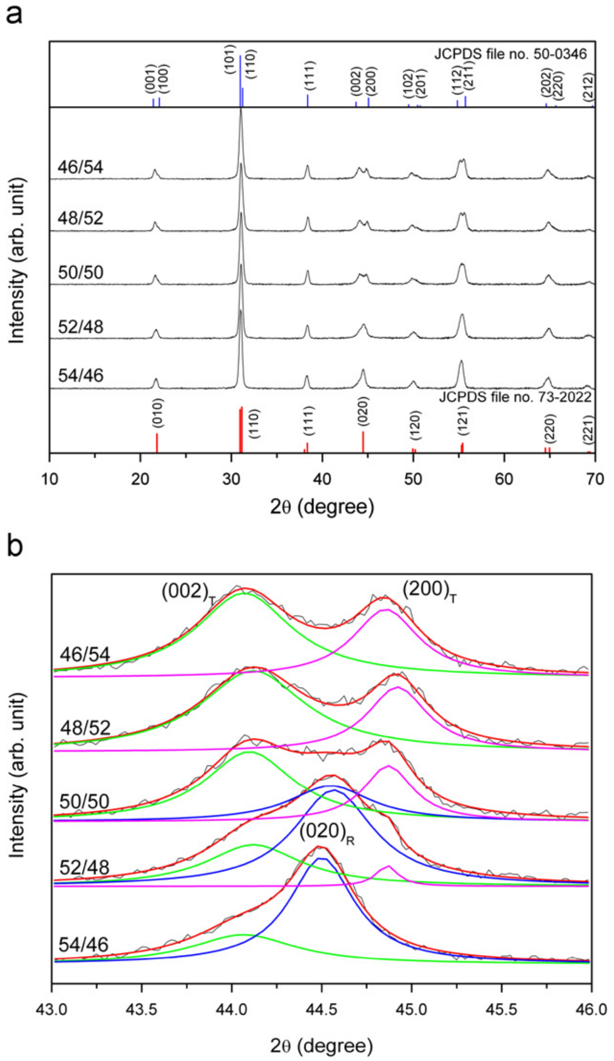

Fig. 1. XRD pattern of $Pb(Zr_{1-x}Ti_x)O_3$–$Pb(Mg_{1/3}Nn_{2/3})O_3$, where $x=0.46$–0.54.

Temperature and frequency dependences of dielectric properties (ε_r and $\tan\delta$) of 0.95PZT − 0.05PMnN ceramics are displayed in Fig. 2. The maximum dielectric constant (ε_{max}) and transition temperature (T_{max}) at 1 kHz are also measured and shown in Fig. 2. The dielectric characteristic shows board peaks at maximum transition temperature with independence on frequency, confirming a normal-like ferroelectric with for all samples possible due to the characteristic of PZT component for 95 mol% in this 0.95PZT − 0.05PMnN ceramics system. In Fig. 2(f), the ε_{max} significantly increases from $x=0.46$ which reaches maximum value at $x=0.52$ and then decreases, clearly indicating the maximum dielectric constant at MPB composition of $x=0.52$. In addition, a clear transition in T_{max} (defined as the temperature at which ε_r is maximum at