Phase Diagram and Dielectric Properties of Pb[Zr_{1-x}(Fe_{0.5}Nb_{0.5})_x]O_3 (0 < x < 0.2) Solid Solutions

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Abstract—The structural, dielectric, and ferroelectric properties of Pb[Zr_{1-x}(Fe_{0.5}Nb_{0.5})_x]O_3 (0 < x < 0.2) solid solutions were investigated. The results were used to assess in detail the phase relations near the morphotropic boundary.

INTRODUCTION

Given that perovskite ceramics are potential materials for electrocaloric cooling applications, we undertook a study of Pb[Zr_{1-x}(Fe_{0.5}Nb_{0.5})_x]O_3 solid solutions, close in composition to the boundary between the ferroelectric (FE) and antiferroelectric (AFE) phase fields. Electrocaloric effect is expected to be most sizeable near electric-field-induced first-order AFE-to-FE phase transitions [1]. In this context, it is of considerable interest to examine the phase relations near PbZrO_3, since the temperature of the AFE-to-FE phase transition decreases sharply for x < 0.1. The Pb[Zr_{1-x}(Fe_{0.5}Nb_{0.5})_x]O_3 solid-solution system was investigated earlier [2–4], but samples were synthesized at 10 at. % intervals, and the composition range x < 0.2 was not examined in sufficient detail.

EXPERIMENTAL

In this work, Pb[Zr_{1-x}(Fe_{0.5}Nb_{0.5})_x]O_3 solid solutions were prepared at 2 at. % intervals (0.2 at. % in the vicinity of the morphotropic boundary) by solid-state reactions from PbO (pure grade), ZrO_2 (pure), Fe_2O_3 (extrapure), and Nb_2O_5 (extrapure). Powder compacts were packed with powder mixtures of the same composition and fired first at t_1 = 700–800 °C for 6 h and then at t_2 = 1100–1270 °C for =1 h in double-wall alumina crucibles under an atmosphere saturated in PbO vapor. We also prepared samples with x = 0.072 containing 2 at. % excess Nb^{5+} and samples containing 0.3–0.5 mol % Li_2O additions. The resultant ceramics were characterized by x-ray diffraction (XRD) and dielectric measurements at 100 kHz. Spontaneous polarization was determined from dielectric hysteresis loop measurements at 50 Hz in electric fields of up to 15 kV/cm. The results were used to construct the T–x phase diagram of the solid-solution system.

RESULTS AND DISCUSSION

XRD analysis indicated the formation of orthorhombic and rhombohedral perovskite solid solutions in

Fig. 1. Composition dependences of (a) T = T_C - T_0 (where T_C and T_0 are the Curie and Curie–Weiss temperatures, respectively), (b) q = I_{206}/I_{200} (SiO_2), (c) ε_{max}, (d) and tan δ; the circles and squares represent the experimental data for the FE–paraelectric and FE_1–FE_2 phase transitions, respectively.
the composition range studied, with a boundary at $x = 0.08$. The volume of the perovskite cell was found to decrease with increasing $x$, in accordance with the smaller size of the Fe and Nb cations as compared to the Zr cation.

Given that PbO may vaporize during high-temperature processing, we assessed the thermal stability of samples with compositions around the morphotropic boundary. It was found that a modified layer whose composition and thickness were dependent on the firing conditions was formed on the sample surface. For example, a lighter colored layer could be seen on the surface of the samples with $x = 0.072$–0.078, fired for $1 \text{ h at } t_2 = 1250^\circ\text{C}$. XRD analysis indicated that the surface layer consisted of a well-crystallized rhombohedral solid solution and a fluorite phase. It was also found that, at $-10\,\mu\text{m depth, the } x = 0.072$ sample consisted of a mixture of the orthorhombic and rhombohedral phases, whereas, $50\,\mu\text{m from the surface, the orthorhombic phase was predominant. The surface layer of the samples obtained at } t_2 = 1270^\circ\text{C with no packing powder contained, for the most part, the fluorite phase. Electron probe x-ray microanalysis showed that the grains situated in the surface layer of these samples contained } 1$–$2 \text{ at. } \% \text{ less Pb than those in the bulk and on the underside. Clearly, these compositional changes are due to PbO vaporization during firing. The likely reason for the formation of the rhombohedral phase is the increase in the content of iron and niobium in the perovskite phase as a result of the precipitation of the Zr-rich fluorite phase. Another possibility is that the local electric field generated by associates of point defects (Pb and O vacancies, impurity atoms) induces

![Fig. 2. Permittivity-vs.-temperature curves for the samples with $x = (1) 0.02$, (2) 0.04, (3) 0.07, (4) 0.2, and (5) 0.06.](image)