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Excellent near-infrared transparency realized in low-symmetry orthorhombic (K,Na)NbO_3-based submicron ceramics

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ABSTRACT

We report that an extraordinary near-infrared transparency, i.e., $T = 91\%$ at ~2000 nm, was achieved in low-symmetry orthorhombic $0.94K_{0.5}Na_{0.5}NbO_3$–$0.06Bi(Zn_{2/3}Nb_{1/3})O_3$ (KNN-0.06BZN) ceramics. The novel transmittance originates from the combination of its submicron-grain size (<0.2 μm) and relaxor behavior ($\gamma = 1.71$). Besides, the retaining of the low-symmetry orthorhombic phase structure assured decent electrical properties in the ceramics: $\varepsilon_{max} = 1337$, and $P_r = 5.28$ μC/cm^2 as $x = 0.06$. Our findings might open a new window for the compatibility of superior transmittance and decent electrical properties.

Because of their unique combination of optical and ferroelectric properties, transparent ferroelectric ceramics can be widely used as electro-optical devices, such as optical shutters and switchers, image memory devices, as well as optical modulation devices [1–9]. Among these ceramics, lead-free KNN-based ceramics have drawn growing attentions since a large d_{33} value of 416pC/N was reported by Saito et al. [5]. However, most of KNN-based ceramics are opaque owing to the strong scattering of light by impurities, micro-pore, crystal structure, grain size, and so on. Therefore, tremendous efforts have been devoted to reduce light scattering, such as decreasing grain size and improving the symmetry of crystal structure [6–11]. Till now, the most feasible method is to alloy another ABO_3-type perovskite, such as A(Me, B)O_3 (A = Ca^{2+}, Sr^{2+}, Ba^{2+}; Me = Zn^{2+}, Mg^{2+}; B = Nb^{5+}, Ti^{4+}) [6,9–13] into KNN matrix to modulate its grain size and phase structure in order to achieve high optical transmittance. However, small grain size and especially the high-symmetric phase structure will deteriorate the electrical properties [6,11]. On this account, how to realize the compatibility of superior transmittance and good electrical properties is very challenging for KNN-based transparent ferroelecric ceramics.

In our previous work, the high transparent $K_{0.5}Na_{0.5}NbO_3$ ceramics with submicron grain size were successfully obtained by Ca $(Zn_{1/3}Nb_{2/3})O_3$ modification [6]. In this work, we moved forward and chose another ABO_3 perovskite-$Bi(Zn_{2/3}Nb_{1/3})O_3$, in order to simultaneously achieve high transmittance and decent electrical properties. The reasoning is as follows: first, Bi^{3+} is of higher valence, thus promising to increase the disorder of the ceramic structure and cause grain size reduction, besides, the low-symmetry orthorhombic structure may be maintained since $Bi(Zn_{2/3}Nb_{1/3})O_3$ and $NaNbO_3$ owns the same phase structure, assuring the relaxor behavior and high temperature dielectrics [14,15].

The ceramics of nominal compositions of (1-x)$K_{0.5}Na_{0.5}NbO_3$-xBi $(Zn_{2/3}Nb_{1/3})O_3$ (x = 0.03, 0.05, 0.06, 0.07, 0.08) were obtained by solid-state reaction and pressureless sintering technology. The raw materials of Na_2CO_3, K_2CO_3, Nb_2O_5, Bi_2O_3, and ZnO (purity of 99.99%) were used to prepare the ceramics. The powders were ball-milled for 24 h and then the slurry was dried. Calcination was performed at 850 °C for 5 h. The calcined powders were then milled again for 24 h. After being dried, the mixed powders were granulated with PVA and then pressed into plate shapes. After vaporizing PVA, the samples were sintered at 1150–1180 °C for 6 h in air. The detailed processes were outlined in our previous work [11].

The transparency, phase structures, microstructures and electrical properties of the ceramics were investigated systematically. The transmittance of the ceramics was characterized by UV–vis-NIR spectroscopy (UV-3600; Shimadzu, Kyoto, Japan). The microstructures were studied by field-emission scanning electron microscopy (FE-SEM, s-4800; Hitachi, Tokyo, Japan). The phase structures of the samples were examined by X-ray diffraction (Mini-Flex600; Rigaku, Tokyo, Japan). The dielectric properties were measured by impedance analyzer (E4980A; Agilent technologies company, Palo Alto, CA), The Polarization–electric filed (P-E) loops were investigated by ferroelectric tester at 1 Hz.

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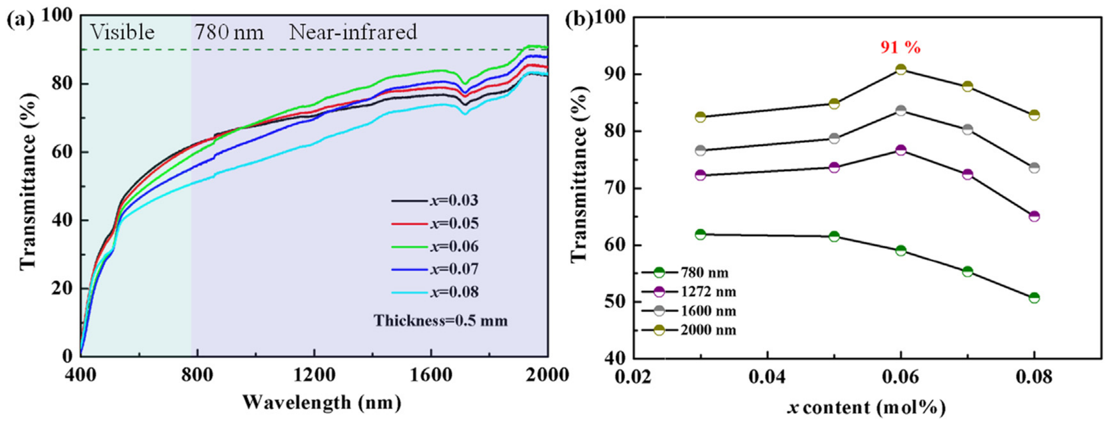

Fig. 1. (a) Transmission spectra of the KNN-*x*BZN ceramics (the dotted green line corresponds to the transmission of 90%), and (b) the optical transmittance at wavelengths 780 nm, 1272 nm, 1600 nm and 2000 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The transmittance of the KNN-*x*BZN ceramics over the entire visible range and near-infrared region are exhibited in Fig. 1(a), all showing good optical transmittance as a function of wavelength. The transmittance (T) clearly depends on x value and increases almost monotonically from the visible range to the near-infrared region. The results display outstanding transparency of all the KNN-*x*BZN ceramics between 400 and 2000 nm, but the rate of increment gradually diverge with x when the wavelength exceeds the visible range. In order to depict the change trend more clearly, Fig. 1(b) shows the optical transmittance vs. x at wavelengths 780 nm, 1272 nm, 1600 nm and 2000 nm, individually. The optical transmittance at 780 nm (visible range) linearly decreases from 62% at $x = 0.03$ to 51% at $x = 0.08$. In contrast, at 1272 nm, 1600 nm, and 2000 nm (near infrared range), the transmittance of the KNN-*x*BZN samples first increases then decreases as the amount of $Bi(Zn_{2/3}Nb_{1/3})O_3$ increases, exhibiting a maximum value at $x = 0.06$. It is worthy emphasizing that the 0.94KNN-0.06BZN ceramic shows marvelous 91% transmission value at ~2000 nm, among the highest values in all reported KNN-based ceramics to the best of our knowledge. The outstanding optical transmittance is mainly attributed to the relatively fine average grain size (AGS) and relaxor behavior, as discussed later.

The scanning electron microscope (SEM) micrographs of the natural surface of the KNN-*x*BZN ceramics are shown in Fig. 2(a)–(e). All the micrographs exhibit dense microstructure, without obvious pore. The inserts of Fig. 2(a)–(e) demonstrate that the KNN-xBZN ceramics are of good transparency since flowers are clearly visible through the disk-like samples. The clarity of the pictures is consistent with the value of the transmittance in the visible range. The high transparency of the ceramics is attributed to the dense microstructure and fine average grain size (AGS). The AGS was measured by analytical software from the surface SEM micrographs of each sample, which are exhibited in Fig. 2(f). The effect of BZN concentration on the AGS followed the unusual trend, i.e. increasing the BZN concentration from $x = 0.03$ to $x = 0.08$ results in an increased AGS from ~151 nm to ~254 nm. Both the high density and the submicron AGS are responsible for the high transparency of the KNN-*x*BZN ceramics, especially for visible range, which can be illuminated by Mie theory [16].

The XRD patterns of KNN-*x*BZN ceramics are shown in Fig. 3, in which all the ceramics present a pure orthorhombic perovskite structure without any secondary phases. The results imply that BZN completely dissolves into KNN lattice and form KNN-*x*BZN solid solution. The crystal phase structure is usually judged by split (200) peak

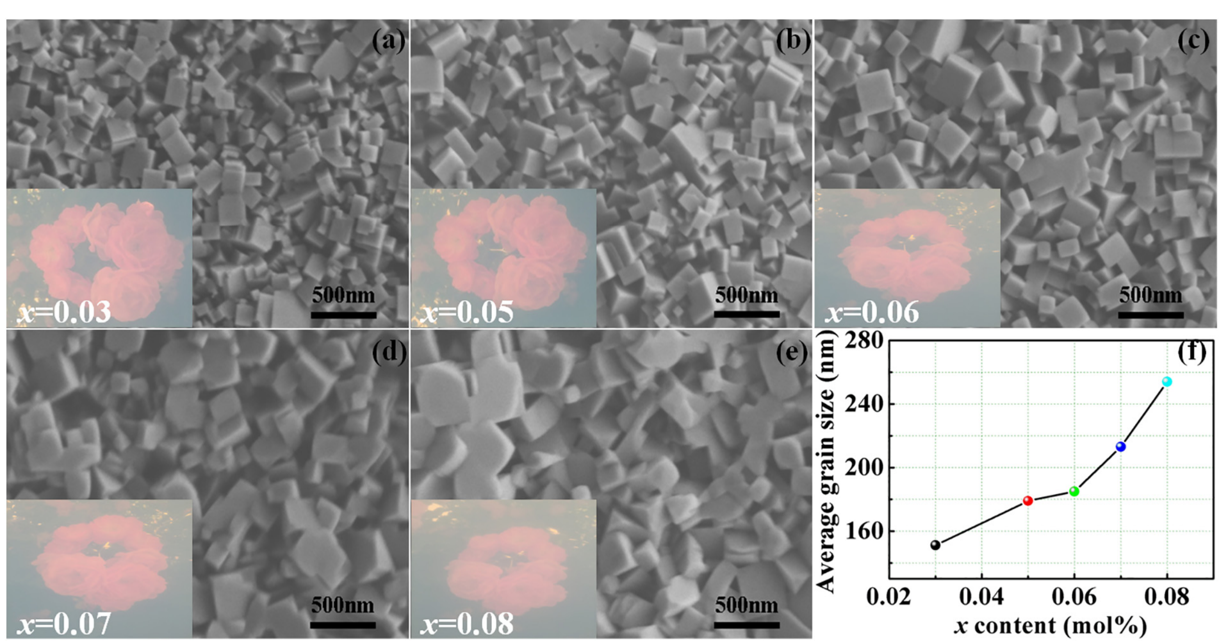

Fig. 2. SEM micrographs on the surface of the KNN-*x*BZN samples: (a) $x = 0.03$, (b) $x = 0.05$, (c) $x = 0.06$, (d) $x = 0.07$, and (e) $x = 0.08$. The insets are the photographs of the transparent KNN-*x*BZN ceramics. (f) The average grain size of the KNN-*x*BZN ceramics.