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Effects of Mn additive on the dielectric and piezoelectric properties of $0.92(Na_{0.5}K_{0.5})NbO_3$-$x$$BaZrO_3$-$(0.08-x)(Bi_{0.5}K_{0.5})TiO_3$ ceramics

NKN-BZ-BKT 系非鉛圧電セラミックスの誘電特性・圧電特性への Mn 添加効果

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1. Introduction

Lead zirconate titanate $Pb(Zr_{1-x}Ti_x)_3$(PZT) has the perovskite ABO_3 structure. It shows high dielectric and piezoelectric properties at room temperature. The piezoelectric properties of PZT could be greatly modified by adding elements[1, 2]. When elements with higher valence than that of Pb^{2+} or $Zr^{4+}(Ti^{4+})$ are added to PZT, vacancies are caused in the perovskite A-site. The A-site vacancies promote the movement of the ions. As a result, the piezoelectric d_{33} constant and the electromechanical coupling coefficient k_p increase, and the mechanical quality factor Q_m decreases. This is called the 'soften' of the piezoelectrics. Oppositely, when elements with lower valence than that of Pb^{2+} or $Zr^{4+}(Ti^{4+})$ are added to PZT, vacancies are caused in the oxygen site. The oxygen vacancies obstruct the movement of the ions. As a result, d_{33} and k_p decrease, and Q_m increases. This is called the 'harden' of the piezoelectrics. When Mn is added, PZT is hardened, that is, d_{33} and k_p decrease, and Q_m increases [1, 2].

Though PZT is a high performance piezoelectric material, it contains a large quantity of toxic lead, thus the development of lead-free piezoelectric ceramics is needed from environmental viewpoint. Recently, much attention has been paid to the lead-free niobate [3, 4]. It is reported that the tetragonal-rhombohedral morphatrobic phase boundary (MPB) has been formed in the $(Na_{0.5}K_{0.5})NbO_3$-$BaZrO_3$-$(Bi_{0.5}K_{0.5})TiO_3$ (BBK) ceramics [5]. And around the MPB, dielectric and piezoelectric properties were enhanced. Moreover, the dielectric and piezoelectric properties of BBK with composition near MPB could be greatly improved by 0.25 wt% MnO_2 additive. However, effects of Mn additive on the dielectric and piezoelectric properties of BBK samples with composition not around the MPB have not been clear.

In the present study, we fabricated $0.92(Na_{0.5}K_{0.5})NbO_3$-$x$$BaZrO_3$-$(0.08-x)(Bi_{0.5}K_{0.5})TiO_3$ and 0.25 wt% MnO_2 added BBK samples. By measuring the temperature dependence of dielectric constant, electromechanical coupling coefficient, piezoelectric d_{33} constant and so on, effects of Mn additive on the dielectric and piezoelectric properties of BBK samples are investigated.

2. Experimental procedure

The powder of $0.92(Na_{0.5}K_{0.5})NbO_3$-$x$$BaZrO_3$-$(0.08-x)(Bi_{0.5}K_{0.5})TiO_3$ (BBK100x) ceramics (x = 0.01～0.07) were made by conventional solid state reaction method using Na_2CO_3, K_2CO_3, Nb_2O_5, $BaCO_3$, ZrO_2, Bi_2O_3, TiO_2, as raw materials. For preparing BBK100x+Mn powder, 0.25 wt% MnO_2 was added to calcined BBK powder and then thoroughly mixed before sintering. The microstructure of the samples was investigated by a scanning electron microscope (SEM). The dielectric constant was measured by an impedance analyzer (Agilent, 4263B) from room temperature to 400 °C. The piezoelectric d_{33} constant was measured by a piezo-d_{33} meter (APC International, Ltd.). The electromechanical coupling coefficient k_p and the mechanical quality factor Q_m was determined by the resonance-anti-resonance method with an impedance analyzer (Agilent, 4294A).

3. Result and Discussion

SEM images of BBK5 and BBK5+Mn samples are shown in Figs. 1(a) and (b), respectively. From the images, it is obvious that there are few pores and the density of the samples is high. The particle size of BBK5 is about 1.0-2.0 μm, however, the particle size of BBK5+Mn is about 2.0–5.0 μm. That is Mn additive promoted the particle size growing. Fig. 2(a) and (b) shows the temperature dependence of the dielectric constant at 100 kHz of BBK and BBK+Mn, respectively. Composition dependence of the phase transition temperatures Tc_{C-T} and Tc_{T-R} is shown in Fig. 3(a). With increasing x, the Tc_{C-T} shifts to the lower temperature side and the Tc_{T-R} shifts to the higher temperature side. For BBK6, the Tc_{T-R} peak is observed near room temperature (Fig. 2(b)). With

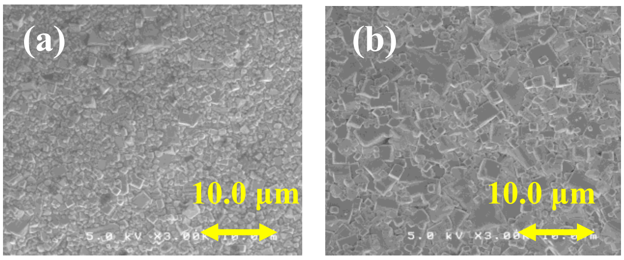

Fig. 1, SEM images of (a) BBK5 and (b) BBK5+Mn samples.

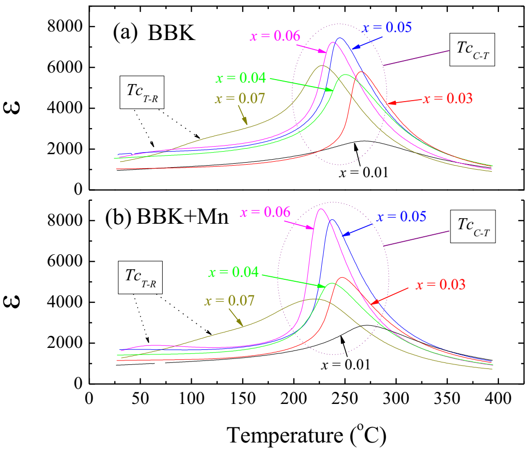

Fig. 2, Temperature dependence of the dielectric constant at 100 kHz of BBK and BBK+Mn samples

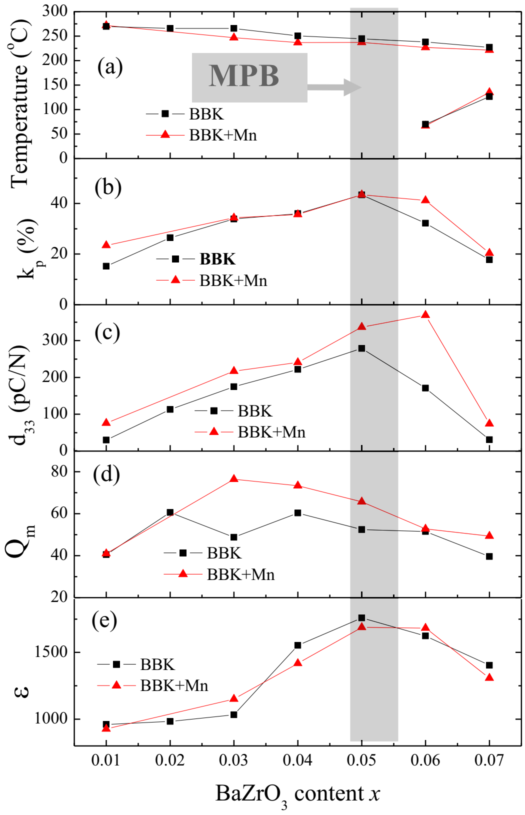

Fig. 3, composition dependence of (a) Phase transition temperatures Tc_{C-T} and Tc_{T-R} (b) electromechanical coupling coefficient k_p, (c) piezoelectric d_{33} constant, (d) mechanical quality factor Q_m, (e) dielectric constant atroom temperature

the addition of Mn, Tc_{C-T} is lowered, whereas Tc_{T-R} shows almost no change.

Figs. 3(b), (c), (d), and (e) show the composition dependence of the electromechanical coupling coefficient k_p, the piezoelectric d_{33} constant, the mechanical quality factor Q_m, dielectric constant at room temperature, respectively. Q_m increased by adding Mn. That is BBK is hardened by adding Mn. This behavior is similar to that of PZT. However, d_{33} and k_p also increased by adding Mn. That is BBK is softened by adding Mn. This behavior is different from that of PZT. In PZT, it is reported that when the particle size increases, the piezoelectric properties increase [6]. From Fig. 1, the particle size has greatly increased by adding Mn. Therefore, the increase of the piezoelectric properties of BBK samples could be attributed to the increase of the particle size.

4. Conclusion

In the present study, we fabricated $0.92(Na_{0.5}K_{0.5})NbO_3$-$x$$BaZrO_3$-$(0.08-x)(Bi_{0.5}K_{0.5})TiO_3$ (BBK) and BBK+Mn ceramics and evaluated their dielectric and piezoelectric properties. It is found that Q_m as well as d_{33} and k_p were increased by adding Mn. The largest increase of d_{33} and k_p was observed at the samples with composition near MPB. In addition, by adding Mn, both the softening and the hardening bahevior were observed in the present study. The hardening bahevior is because of the oxygen vacancies caused by Mn additive. Whereas the softening behevior is attributed to the increase of the particle size by adding Mn.

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