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Enhanced piezoelectric and ferroelectric properties in Mn-doped $Na_{0.5}Bi_{0.5}TiO_3-BaTiO_3$ single crystals

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High piezoelectric and ferroelectric properties have been found in Mn-doped $Na_{0.5}Bi_{0.5}TiO_3-BaTiO_3$ single crystals, which were grown by a top-seeded solution method. The electrical resistivity, dielectric constant, and ferroelectric and piezoelectric properties were all found to be notably enhanced by Mn. The piezoelectric constant d_{33} and electromechanical coupling coefficients k_t and k_{31} were found to be as high as 483 pC/N, 0.56, and 0.40, respectively. These values are much higher than those previously reported for Pb-free piezoelectric crystals, demonstrating the real potential for alternative lead-free systems for sensor and piezoelectric applications. © *2009 American Institute of Physics*. [doi:10.1063/1.3222942]

Lead-based perovskite solid solutions of $PbZrO_3-PbTiO_3$ (PZT) have been widely used for piezoelectric devices due to their large piezoelectric constants at relatively high temperatures.[1,2] Superior piezoelectric properties are observed near a morphotropic phase boundary. Recently, lead-free piezoelectrics have been attracting more attention from an environmental perspective. Although there has been a concerted effort to develop lead-free alternatives, no effective system has yet been found. Solid solutions of $Na_{0.5}Bi_{0.5}TiO_3-BaTiO_3$ (NBT-BT) are recognized as a leading candidate for such Pb-free alternatives, as they have relatively high piezoelectric constants and Curie temperatures.[3–5] The electric properties of NBT-BT solid solutions might obviously be enhanced by doping and by optimizing preparation conditions.[6,7] Values for the piezoelectric constant d_{33} of NBT-BT ceramics and single crystals have been reported to be as high as 205 (Ref. 6) and 280 pC/N,[7] respectively. However, these properties are still notably inferior to that of lead-based ones. In addition, relatively high leakage currents due to defects are another problem to overcome in NBT-BT, which can interfere with poling and polarization switching. Modest concentrations of Mn dopants have been reported to be an effective method by which to enhance the resistivity of lead-based materials.[8] Please note that the piezoelectric properties of NBT-BT ceramics doped with Mn have previously been reported.[9–11]

Here, Mn-doped NBT-BT single crystals with high piezoelectric and ferroelectric properties were grown by a carefully controlled top-seeded solution growth (TSSG) method. It is worth emphasizing that the dc electrical resistance was notably increased by Mn substitution, and that values of d_{33} and the thickness electromechanical coupling factor (k_t) for ⟨001⟩ oriented crystals was, respectively, found to be as high as 483 and 0.56 pC/N. In addition, these crystals had a remnant polarization of $P_r=45.3\ \mu C/cm^2$.

Single crystals of Mn-doped NBT-BT were grown by a self-flux technique. Raw materials of Na_2CO_3 (99.95%), Bi_2O_3 (99.99%), TiO_2 (99.99%), $BaCO_3$ (99.99%), and MnO_2 (99.9%) were mixed according to a stoichiometric ratio of $(Na_{0.5}Bi_{0.5})_{0.9}-Ba_{0.1}TiO_3+1$at% MnO_2, with a 20 wt % excess of Na_2CO_3 and Bi_2O_3 as a self-flux. The mixed raw materials were put into a platinum crucible and heated to 1100 °C for 10 h to decompose the carbonates. Single crystals of Mn-doped NBT-BT were grown by a TSSG method, both Pt wires [designated as Mn:NBT-BT(Pt)] and small ⟨001⟩ oriented NBT-BT single crystals (designated as Mn:NBT-BT) were used as seeds. The concentration of Ba and Mn ions in the crystals were determined carefully by inductive coupled plasma atomic emission spectrometry (ICP-AES). ⟨001⟩ oriented wafers of Mn-doped NBT-BT single crystals were cut into dimensions of $5\times5\times0.5\ mm^3$ and $8\times2\times0.5\ mm^3$, and silver electrodes were coated on the major surfaces. All crystals were poled in silicon oil at 80 °C under a dc field of 3 kV/mm for 15 min. The dielectric properties of poled and unpoled samples were measured on heating at frequencies of 1, 10, and 100 kHz using a HP4192A *LCR* meter. The values of d_{33} were measured by a quasistatic Berlincourt-type meter, and the electromechanical coupling factors k_t and k_{31} were determined by a resonance method using a HP4192A impedance analyzer. Temperature-dependent dielectric constant studies were done using a *LCR* meter (HP 4284A). The polarization (*P-E*) and strain (*S-E*) hysteresis loops were measured by a modified Sawyer–Tower circuit and a linear variable differential transducer (LVDT).

Photos of as-grown Mn-doped crystals are shown in Fig. 1. Analysis by ICP-AES of as-grown crystals revealed that the concentrations of Ba and Mn ions were 5.6 and 0.14 at. %, respectively. The results indicate that Ba ions experienced notable composition segregation during crystal growth. Pure NBT-BT crystals with the same concentration of Ba ions were grown for comparisons.

Figure 2(a) shows the temperature and frequency dependence of ε_r and tan δ for a poled ⟨001⟩ oriented Mn:NBT-BT

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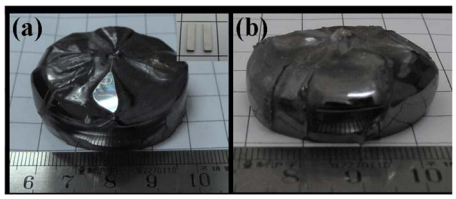

FIG. 1. (Color online) Photos of Mn-doped NBT-BT single crystals and samples (a) grown using ⟨001⟩ oriented seed (Mn:NBT-BT) and (b) grown using Pt wire as seed [Mn:NBT-BT(Pt)].

crystal. Two abnormal dielectric peaks can be seen, as indicated by T_d and T_m. The depolarization temperature T_d plays an important role with regard to practical applications of NBT-BT single crystals, as it was previously been reported as the temperature of a ferroelectric→antiferroelectric transformation,[3] whereas T_m that of an antiferroelectric →paraelectric one. In addition, the dielectric peak at T_d is frequency dispersive, implying a relaxorlike character. Recently, other perspectives of the nature of the phase transition at T_d were presented,[12–14] and clearly further studies concerning the mechanism of depolarization are needed.

Figure 2(b) shows the low frequency (100–500 Hz) dielectric constant as a function of temperature for NBT-BT, with the inset showing that for Mn:NBT-BT. These data reveal a dramatically enhanced dielectric constant for NBT-BT in the temperature range of 300–600 °C, yielding values in excess of 10^5, which were extremely frequency dispersive. These data evidence the presence of a space charge conduction mechanism at elevated temperatures as previously reported,[12] which results in correspondingly high loss factors. It is important to note in this temperature range of 300–600 °C, that Mn was extremely effective in suppressing such conduction effects, as can be seen in the inset. In fact, for Mn:NBT-BT, no evidence of enhanced permittivity was observed in this elevated temperature range. Rather, the maximum dielectric constant was only 6000, which was ~15× lower than that of unmodified NBT-BT. Space charge in NBT-BT crystals may result from bismuth V'''_{Bi} and oxygen $V^{\cdot\cdot}_O$ vacancies, due to Bi_2O_3 volatility during crystal growth, i.e., $2Bi^{3+}+3O^{2-}\leftrightarrow 2V'''_{Bi}+3V^{\cdot\cdot}_O+Bi_2O_3$. When Mn is incorporated onto the A-sites of NBT-BT, the concentration of $V^{\cdot\cdot}_O$ will be decreased as $2Mn^{3+}+2Bi^{3+}+3O^{2-}\leftrightarrow 2Mn^{\times}_{Bi}+Bi_2O_3$. Accordingly, space charge conduction might be suppressed by Mn substitution, enhancing the high temperature dc electrical resistivity and decreasing the leakage current density.[15–17]

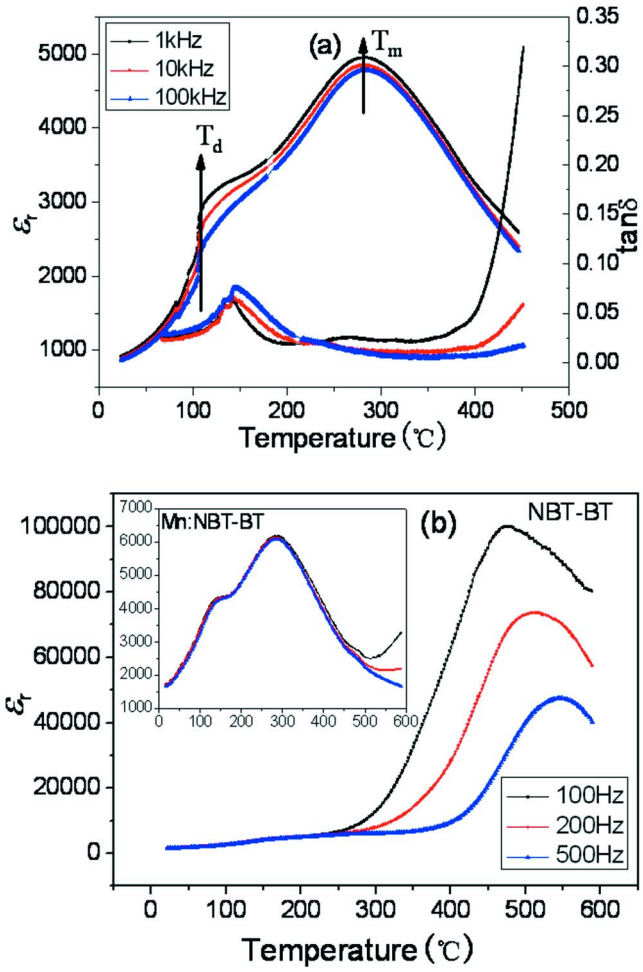

FIG. 2. (Color online) Dielectric constant of ⟨001⟩ oriented poled Mn:NBT-BT and NBT-BT crystal samples as a function of temperature. (a) Mn:NBT-BT at the frequencies of 1, 10, and 100 kHz. (b) Low frequency (100–500 Hz) dielectric constant of Mn:NBT-BT and NBT-BT.

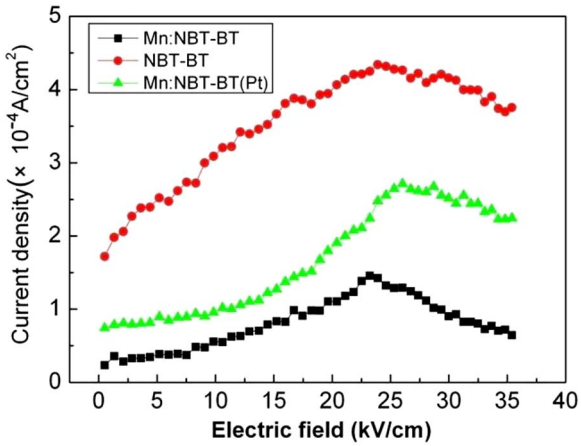

FIG. 3. (Color online) Current density as a function of applied electric field along the [001] direction measured at room temperature.

Figure 3 shows the leakage current density J as a function of an electric field applied along [001] for as-grown Mn:NBT-BT and NBT-BT crystals. It can be seen that the leakage current density of Mn:NBT-BT was about one order of magnitude lower than that of undoped NBT-BT. Peaks of leakage current density for both Mn-doped and undoped NBT-BT (previously unpoled) are evident near 2.5 kV/mm, which is close to E_c where ferroelectric domain switching occurs. Such an enhancement in electrical resistivity by Mn substitution should notably improve the high field electrical strength of the crystal and enable the poling of ferroelectric crystals with high coercive fields.

The P-E and S-E hysteresis loops at room temperatures under bipolar drive for ⟨001⟩ Mn:NBT-BT crystals are shown in Figs. 4(a) and 4(b), respectively. The remnant polarization was P_r=45.3 μC/cm^2 for Mn:NBT-BT (i.e., grown with NBT-BT seeds), which was larger than the 35 μC/cm^2 of Mn:NBT-BT(Pt) (i.e., grown with Pt-wire seeds). Because of improvement in crystal quality and a decrease in leakage current density, higher remnant polarizations P_r were found for Mn:NBT-BT relative to Mn:NBT-BT(Pt). We also found that the P-E hysteresis loops of Mn: NBT-BT had higher

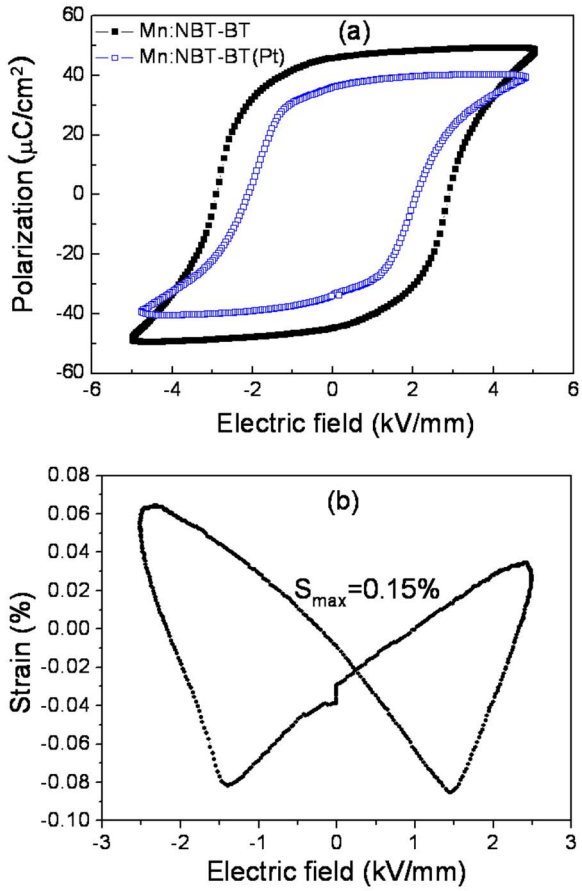

FIG. 4. (Color online) (a) *P-E* hysteresis loops for Mn:NBT-BT samples compared with Mn:NBT-BT(Pt) one; (b) strain vs bipolar electric field curve for Mn:NBT-BT crystals at room temperatures.

saturation polarizations than that previously reported for NBT-BT.[7] Figure 4(b) shows the *S-E* curve for Mn:NBT-BT, where a maximum strain of 0.15% was found under 25 kV/cm. A comparative summary of the piezoelectric and ferroelectric properties for Mn:NBT-BT crystals with other piezoelectric materials is given in Table I. This summary clearly shows that Mn:NBT-BT single crystals have notably superior electromechanical properties relative to that previously reported for PZT4 ceramics and for NBT-BT crystals.[7] For our Mn:NBT-BT crystals, values of d_{33}, k_t, and k_{31} of 483 pC/N, 0.56, and 0.40 were, respectively, found. We believe that the reasons for our Mn:NBT-BT crystals having superior electromechanical properties are improved crystal quality, reduced leakage currents, and defect-domain interactions in the ⟨001⟩ poled condition.

TABLE I. Piezoelectric and ferroelectric properties of PZT4 ceramics and NBT-BT, Mn:NBT-BT(Pt), and Mn:NBT-BT single crystals.

	d_{33} (pC/N)	k_t (%)	k_{31} (%)	d_{31} (pC/N)	P_r μC/cm^2	E_c (kV/mm)
PZT4	250	48	33	170	⋯	⋯
NBT-BT[a]	280	⋯	⋯	⋯	16.44	3.27
Mn:NBT-BT(Pt)	287	56	⋯	⋯	35	2.67
Mn:NBT-BT	483	55.6	39.7	115	45.3	2.91

[a]Reference 7

In summary, Mn-doped NBT-BT single crystals were grown by TSSG. These crystals had superior piezoelectric and ferroelectric properties. We found values for d_{33} as high as 483 pC/N, which was nearly double that of prior reports for NBT-BT. In addition, the leakage current of NBT-BT crystals decreased notably upon Mn substitution, allowing for a more complete poling. Our findings demonstrate the real possibility of developing Pb-free NBT-BT crystals as alternatives to conventional PZT piezoelectrics.

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[1]G. H. Haertling, J. Am. Ceram. Soc. **82**, 797 (1999).
[2]L. H. Luo, H. Zhu, C. S. Zhao, H. X. Wang, and H. S. Luo, Appl. Phys. Lett. **90**, 052904 (2007).
[3]T. Takenaka, K. Maruyama, and K. Sakata, Jpn. J. Appl. Phys., Part 1 **30**, 2236 (1991).
[4]Y. M. Chiang, G. W. Farrey, and A. N. Soukhojak, Appl. Phys. Lett. **73**, 3683 (1998).
[5]B. J. Chu, D. R. Chen, G. R. Li, and Q. R. Yin, J. Eur. Ceram. Soc. **22**, 2115 (2002).
[6]T. S. Zhou, R. X. Huang, X. Z. Shang, F. Peng, J. Y. Guo, L. Y. Chai, and H. S. Gu, Appl. Phys. Lett. **90**, 182903 (2007).
[7]W. W. Ge, H. Liu, X. Y. Zhao, B. J. Fang, X. B. Li, F. F. Wang, D. Zhou, P. Yu, X. M. Pan, D. Lin, and H. S. Luo, J. Phys. D: Appl. Phys. **41**, 115403 (2008).
[8]L. H. Luo, D. Zhou, Y. X. Tang, Y. M. Jia, H. Q. Xu, and H. S. Luo, Appl. Phys. Lett. **90**, 102907 (2007).
[9]G. F. Fan, W. Z. Lu, X. H. Wang, and F. Liang, J. Mater. Sci. **42**, 472 (2007).
[10]M. K. Zhu, L. Y. Liu, Y. D. Hou, H. Wang, and H. Yan, J. Am. Ceram. Soc. **90**, 120 (2007).
[11]X. Y. Zhou, H. S. Gu, Y. Wang, W. Y. Li, and T. S. Zhou, Mater. Lett. **59**, 1649 (2005).
[12]S. E. Park and S. J. Chung, J. Am. Ceram. Soc. **79**, 1290 (1996).
[13]G. O. Jones and P. A. Thomas, Acta Crystallogr., Sect. B: Struct. Sci. **58**, 168 (2002).
[14]C. W. Tai, S. H. Choy, and H. L. W. Chan, J. Am. Ceram. Soc. **91**, 3335 (2008).
[15]H. Nagata and T. Takenaka, J. Eur. Ceram. Soc. **21**, 1299 (2001).
[16]D. Szwagierczak, and J. Kulawik, J. Eur. Ceram. Soc. **25**, 1657 (2005).
[17]Y. Kizaki, Y. Noguchi, and M. Miyayama, Appl. Phys. Lett. **89**, 142910 (2006).