

Effect of NiO on Microstructure and Properties of PMN-PT-BT Ceramics Prepared by Mixed Oxide Method

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ABSTRACT

Effects of NiO were studied in aspects of dielectric properties and microstructure of $0.96(0.91\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.09\text{PbTiO}_3)-0.04\text{BaTiO}_3$ (PMN-PT-BT, PBT). The PBT was prepared by a conventional mixed oxide method using $(\text{MgCO}_3)_4 \cdot \text{Mg}(\text{OH})_2$ instead of MgO through Lewis acid-base interaction. NiO was added in the range of 0.5 to 3.0 wt% as thermally decomposable $2\text{NiCO}_3 \cdot 3\text{Ni}(\text{OH})_2$ and it seemed to enhance densification to a large extent below 1000°C. But all the systems gave rise to ceramics with almost same relative sintered density of 96% by sintering at 1000°C for 2 h. But it turned out that the addition of NiO was detrimental to dielectric constant but beneficial to the loss of dielectric constant.

Key words : PMN-PT-BT, Dielectric properties, Low temperature sintering

1. Introduction

Many modified relaxor materials based on $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ have been studied to optimize their achievable dielectric and electrostrictive properties for various applications such as capacitors, transducers, actuators, etc.¹⁻⁶⁾ Studies on PMN synthesis have shown that the introduction of Mg in an early-formed P_2N pyrochlore is the critical step in the perovskite formation mechanism. Therefore it was proposed to synthesize the MgNb_2O_6 columbite precursor at ~1200°C and then followed by the reaction with PbO at ~800°C, which is known as the columbite process and has been commonly used to synthesize Pb-based niobium containing complex perovskite compounds.^{1,3)} Such prepared perovskite single phase PMN-PT powder still sinters at ~1200°C. As a consequence studies on developing preparation methods for low-temperature-sinterable PMN-PT systems have been pursued.⁷⁻¹³⁾ Besides, efforts with additives were also reported. For examples, a modified system of PMN-PT-BT with excess MgO and $4\text{PbO}/\text{B}_2\text{O}_3$ sintered at 1050°C.¹⁴⁾ Addition of MgO and PbO to the PMN-PT solid solution lowered sintering temperature to 1000°C.¹⁵⁾ Addition of small amount of Ag, Pd, Ag/Pd enhanced the sintering behavior of PMN-PT with improved dielectric constant.¹⁶⁻¹⁹⁾ Pilgrim *et al.* also studied on dielectric and electromechanical properties of PMN-PT-BT chemically modified with small amount of additives such as TiO_2 , BaO, ZnO, SrO by a particulate coating process and consolidation performed at

1200°C for 4 h.²⁰⁾

In the present study we developed a method to synthesize PMN-PT-BT with single perovskite phase by a conventional mixed oxide method and also studied NiO as a sintering additive.

2. Experimental Procedure

The composition of the PMN-PT-BT is $0.96(0.91\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.09\text{PbTiO}_3)-0.04\text{BaTiO}_3$ and called PBT hereafter. Starting materials used in the present study were PbO (99.9% purity, Aldrich Chem. Co., U.S.A.), Nb_2O_5 (99.9% purity, Aldrich Chem. Co.), TiO_2 (anatase, 99.9% purity, Aldrich Chem. Co.), BaCO_3 (99.80% purity, Sakai Chemical Co., Japan), $(\text{MgCO}_3)_4 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ (99% purity, Aldrich Chem. Co.), $2\text{NiCO}_3 \cdot 3\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ (99% purity, Aldrich Chem. Co.) and isopropyl alcohol.

It was prepared as the following: appropriate amounts of PbO (0.373 mole), BaCO_3 (0.016 mole), $(\text{MgCO}_3)_4 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ (0.024 mole), TiO_2 (0.005 mole) and Nb_2O_5 (0.113 mole) were placed with isopropyl alcohol in a polypropylene bottle and milled using zirconia balls ($\phi = 5$ mm) for 24 h. The slurry was rotary evaporated to remove the solvent. About 20 mg of the dried PBT precursor was heated in a Pt/Rh crucible to 950°C with a heating rate of 10°C/min under flowing air using TG/DSC (Model 409STA, Netzsch Co., GmbH). The dried powders were heated at various temperatures between 500°C and 900°C for 2 h, and then subjected to SEM (Model 3000, Hitachi Co., Japan) and XRD analysis. It was taken between $2\theta = 20 - 70^\circ$ with a scanning rate of $2^\circ/\text{min}$ by X-ray diffractometer (Model D/Max-3A, Rigaku Co., Japan). $\text{CuK}\alpha$ was used with a graphite monochromator filter at 30 kV and 20 mA.

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Consolidation study was tried with the noncrystalline powder. Since the weight loss was almost complete by 500°C, the PBT precursor was calcined at 500°C for 2 h and mixed with the NiO precursor at the ratios of 0.5, 1.0, and 3.0 wt% by ball milling in isopropyl alcohol for 6 h. and then dried. The dried powder was passed through a 100 mesh sieve and then uniaxially pressed into pellets of ~10 × 3 mm under 2000 kg/cm². They were sintered on a platinum foil covered with PbZrO₃ powder in an enclosed alumina crucible from 850°C to 1000°C for 2 h with heating and cooling rate of 5°C/min. The sintered density was measured by the Archimedes method in water. Dielectric constant and loss of dielectric constant were measured at 1 kHz using a LF Impedance Analyzer (Model 4192A, Hewlett-Packard Inc., U.S.A.). Prior to the dielectric measurements, samples were polished to obtain a flat and parallel surface and electroded with a silver paste by screen printing. Electrical resistivity was measured at room temperature using a picoammeter (Model 4339A, Hewlett-Packard Inc., U.S.A.) at 25 V.

3. Results and Discussion

The PBT precursor was simply prepared by a conventional

mixed oxide method using (MgCO₃)₄ · Mg(OH)₂ · 5H₂O instead of MgO through Lewis acid-base chemistry in a similar way as previously reported 65PMN-35PT.²¹ It showed almost complete weight loss by 500°C on its TG curve as

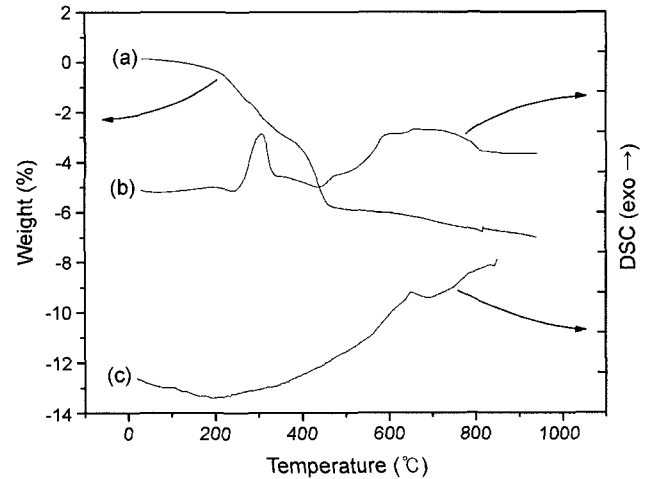
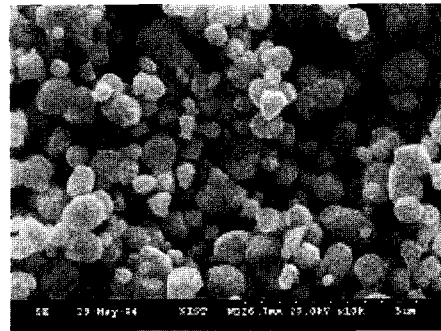
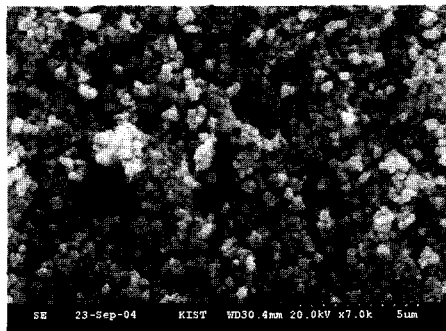
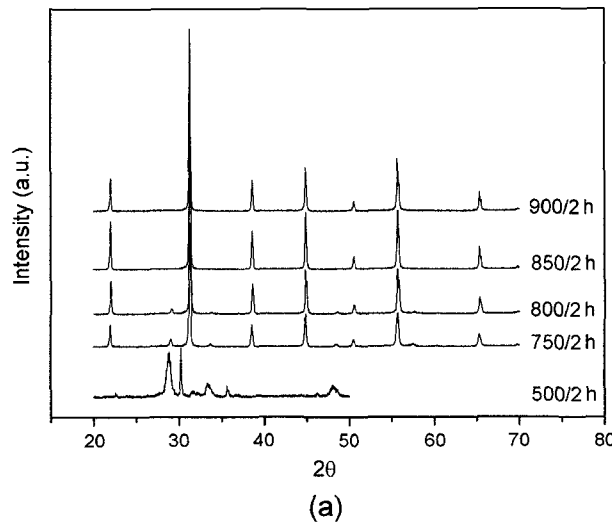


Fig. 1. TG and DSC curves of : (a, b) PBT precursor and (c) a mixture of PbO, Nb₂O₅, and MgO heated at a heating rate of 10°C/min.



(b)

(c)

Fig. 2. (a) development of XRD patterns of the PBT precursors heated at various temperatures and SEM images of the PBT precursors heated at: (b) 500°C and (c) 850°C.

shown in Fig. 1. It also showed a big broad exothermic peak around 700°C which was not observed in the case of the PMN precursor prepared by a mixed oxide method. The peak implied that there were phase transformations, therefore the precursor was heat treated at various temperatures to see a perovskite phase. The results shown in Fig. 2 demonstrate that a single perovskite phase was obtained at 850°C. It was noticeable that the calcined powder was discrete with size of 0.3~1 μm. Since the PBT is known sinterable at around 1200°C, addition of NiO was attempted to lower sintering temperature. Thermally decomposable $2\text{NiCO}_3 \cdot 3\text{Ni(OH)}_2 \cdot 4\text{H}_2\text{O}$ compound was added when the precursor was prepared by mixing the starting chemicals to see the effect on calcination temperature for pure perovskite single phase. The addition of 0.5 wt% NiO barely affected on heating temperature for the pure phase formation, but 1.0 and 3.0 wt% NiO lowered the temperature to 800°C as shown in Fig. 3. The peak of NiO appeared on its XRD pattern when 3.0 wt% was used, but not in the cases of 0.5 wt% and 1.0 wt% NiO were employed, which was probably due to small amount of NiO. The SEM pictures showed that the particles were discrete and grew a little bigger and more uniform as the amount of NiO was increased. It seemed that NiO diffused to the PBT at a small extent and then the excess NiO precipitates as 0.1~0.2 μm on the surface of PBT particles as shown in Fig. 3. Since it did not seem feasible to make NiO dispersed in nanosize by sintering the above composite powders, attempts were made to make nanosize NiO

particles dispersed in sintered ceramics by mixing the Ni compound with the precalcined PBT powder at 500°C for 2 h.

As the amount of NiO was increased from 0 to 3.0 wt% below 1000°C, densification was enhanced substantially but dielectric constant was adversely decreased as shown in Fig. 4. However almost same relative sintered density, 96%, was obtained for all the systems by sintering at 1000°C for 2 h, but dielectric constants at room temperature were depended on the amount of NiO. Without the additive the dielectric

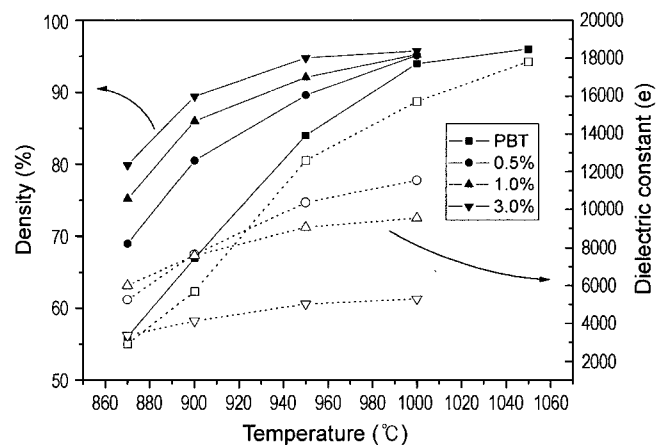


Fig. 4. Relative sintered density and dielectric constant of the PBT with various amount of NiO sintered at various temperatures for 2 h.

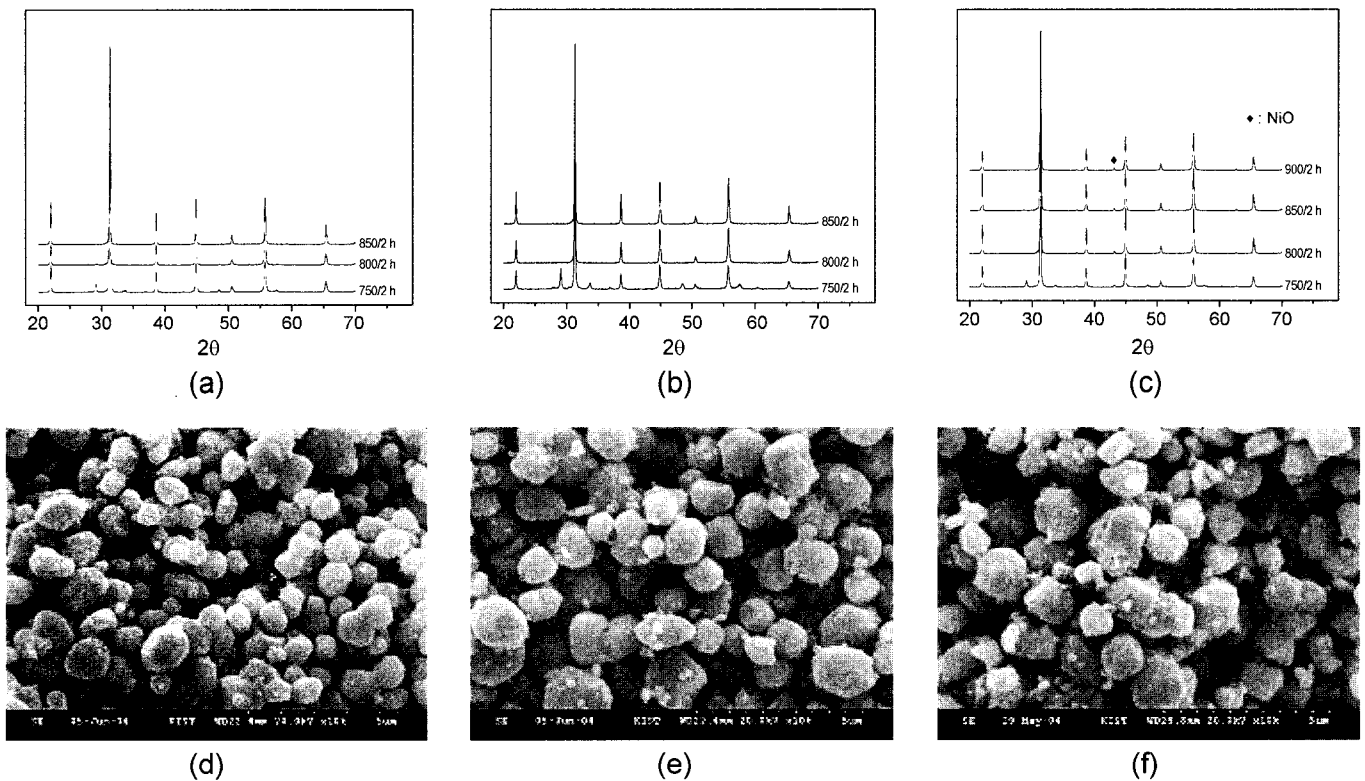


Fig. 3. Development of XRD patterns of the PBT precursors with various amount of NiO; (a) 0.5 wt%, (b) 1 wt%, and (c) 3 wt%, and SEM images of : (d) calcined (a) at 850°C, (e) calcined (b) at 850°C, and (f) calcined (c) at 800°C.

constant was high, 16000, but it decreased dramatically to 11500, 9500, and 5300 for 0.5 wt%, 1.0 wt%, and 3.0 wt% of the additive, respectively. The dielectric loss was reduced as the sintering temperature and the amount of NiO were increased as shown in Fig. 5. Fig. 6 shows microstructures of the samples sintered at 1000°C for 2 h. Addition of 0.5 wt% NiO resulted in substantial reduction of grain size from 2~6 μm to 2~3 μm. As the amount of NiO increased to 1.0 and 3.0 wt%, the grains became more homogeneous and smaller, 1.5~2.5 μm, 1~2 μm, respectively. NiO particles were distributed at grain boundaries and grew larger from 0.4 μm to 0.7 μm as the amount of NiO was increased. From the above observations NiO worked as a good inhibitor for grain growth and enhanced densification when small amount was used. But NiO cannot be restrained as nano-size by a usual simple distribution method. Therefore strategies are needed to suppress migration of NiO by surface

modification. Such attempts are undergoing with MgO sol in our lab.

4. Conclusions

PMN-PT-BT (PBT) complex perovskite compound was prepared as agglomerate-free submicron size by a conventional mixed oxide method with $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$ instead of MgO through Lewis acid-base reaction. Single pure perovskite phase PBT powder was obtained by calcination at 850°C for 2 h. Addition of 1.0 or 3.0 wt% NiO lowered the formation temperature of pure perovskite phase to 800°C and formed NiO particles of 0.1 – 0.2 μm on the surface of PBT particles. Consolidation study with PBT powder calcined at 500°C showed that a small amount of NiO enhanced densification to a large extent below 1000°C and excess NiO precipitated at grain boundaries resulting in grain growth inhibition. Presence of NiO particles in submicron size seemed detrimental to dielectric constant.

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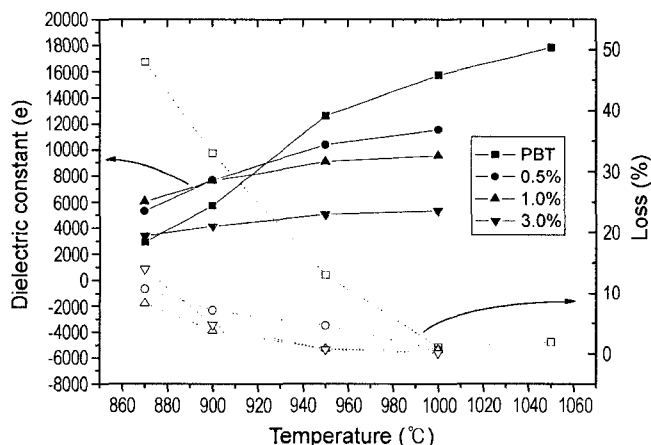


Fig. 5. Dielectric constant and loss of dielectric constant of the PBT with various amount of NiO sintered at various temperatures for 2 h.

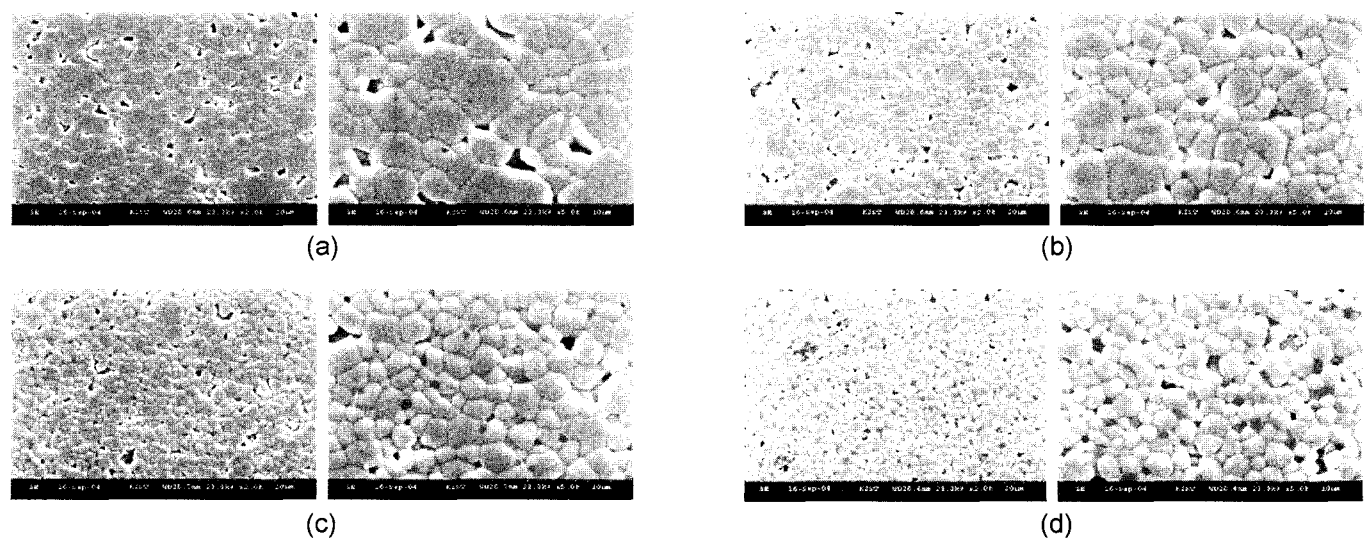


Fig. 6. SEM images of polished and thermally etched surfaces of the PBT sintered with various amounts of NiO of: (a) 0, (b) 0.5 wt%, (c) 1 wt%, and (d) 3 wt% at 1000°C for 2 h.

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