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Ceramics International 31 (2005) 1025–1029

CERAMICS INTERNATIONAL

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Effects of chemical additives on high-field electromechanical properties of PMN–PT–BT ceramics

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Received 25 March 2004; received in revised form 22 April 2004; accepted 5 November 2004
Available online 22 January 2005

Abstract

A chemical additive method using sol–gel reactions was used to modify the composition and resultant properties of a commercially available $0.96(0.91Pb(Mg_{1/3}Nb_{2/3})O_3–0.09PbTiO_3)–0.04\ BaTiO_3$ (PMN–PT–BT) ceramic. Without an additional ball-mixing process, several combinations of minor additives such as Fe, Ba, Sr, Zn, and Ti were incorporated by the chemical method. Weak- and high-field characteristics including dielectric properties, induced strain and polarization, and associated hystereses were evaluated for the samples sintered at 1200 °C for 4 h. All properties were found to depend on the chemical additives and temperature. Especially, the temperature dependence of high-field characteristics revealed different behavior from that reported for conventionally prepared samples. For example, the samples containing 0.5 wt.% SrO, 0.5 wt.% ZnO, and 0.5 wt.% TiO_2 did not exhibit a transition to piezoelectric behavior at the temperature expected from the dielectric measurements. Overall, the coating process has been successfully used to modify, and in some cases, enhance the high-field characteristics of PMN-based ceramics for electromechanical uses.

Keywords: A. Sol–gel processes; C. Dielectric properties; D. Niobates; E. Actuators

1. Introduction

$Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and related materials are well known for dielectric and electromechanical applications [1–6]. Several promising electromechanical properties like ~0.1% longitudinal strain (>0.03% transverse strain) at 1 MV/m and 0.1 Hz, and <0.05 tan δ at the temperature of peak weak-field permittivity T_{max} and 1 kHz have been reported [7,8]. These properties constitute enabling performance for a wide variety of military and commercial products.

The chemical modification method for incorporating sol–gel derived additives has been investigated to improve the performance of electronic ceramics [9–11]. Small amounts of the chemically-derived additives tend to coat particle surfaces of the calcined base materials at the nanoscale. Basically, they can contribute to homogeneity of the additive distribution over the sample after firing. They may also lead to more desirable microstructural characteristics, depending on the type of additives and base materials. The importance of the chemical additive method should be greater for more microstructure-sensitive materials such as barium titanates or ferrites [11,12]. In our previous work [13], this method was applied to a PMN-based relaxor composition, $0.96(0.91Pb(Mg_{1/3}Nb_{2/3})O_3–0.09PbTiO_3)–0.04\ BaTiO_3$, possessing 310 microstrain at 1 MV/m and 0.0029 tan δ at the temperature of peak weak-field permittivity T_{max} (~18,600 at 1 kHz). Several additives such as Sr, Ba, Ti, Zn, and Fe were selected for detailed study. The resultant high-field characteristics showed some abnormal behavior, which differs from the case of conventionally batch-mixed samples. This work explores the novel chemical additive method by using different sets of additives, with an emphasis on the temperature dependence of high-field characteristics.

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0272-8842/$30.00
doi:10.1016/j.ceramint.2004.11.001

Table 1
Additive composition, bulk density and average grain size for the 0.96(0.91Pb($Mg_{1/3}Nb_{2/3}$)O_3–0.09$PbTiO_3$)–0.04 $BaTiO_3$ samples chemically-modified and sintered at 1200 °C for 4 h (theoretical density of the base composition ~8.00 g/cm^3)

Sample ID	Additive composition	Bulk density (g/cm^3)	Grain size (μm)
NO[a]	No additives	7.60	2.8
F5B5T5	0.5 wt.% Fe_2O_3, 0.5 wt.% BaO and 0.5 wt.% TiO_2	7.67	2.6
B5Z5T5	0.5 wt.% BaO, 0.5 wt.% ZnO and 0.5 wt.% TiO_2	7.61	3.8
S5Z5T5	0.5 wt.% SrO, 0.5 wt.% ZnO and 0.5 wt.% TiO_2	7.63	3.7

[a] [13].

Table 2
Dielectric properties measured at 1 kHz for the 0.96(0.91Pb($Mg_{1/3}Nb_{2/3}$)O_3–0.09$PbTiO_3$)–0.04 $BaTiO_3$

Sample ID	k' at RT	tan δ at RT	k'_{max}	tan δ at k'_{max}	Temperature at k'_{max} (°C)
NO[a]	18,600	0.029	18,600	0.029	25
F5B5T5	22,600	0.063	23,200	0.031	31
B5Z5T5	20,800	0.070	22,200	0.037	31
S5Z5T5	22,400	0.046	22,600	0.040	26

Samples sintered at 1200 °C for 4 h (RT: room temperature ~25 °C).
[a] Ref. [13].

2. Experimental procedure

A chemical method was used to modify a commercially-available PMN-based relaxor composition, 0.96(0.91Pb($Mg_{1/3}Nb_{2/3}$)O_3–0.09$PbTiO_3$)–0.04 $BaTiO_3$ (Active Signal Technologies, MD, USA). The chemical method utilizes sol–gel reactions between the precursors of given additives such as Ti, Zn, Fe, Ba, and Sr. Table 1 represents the additive compositions and corresponding precursors, which were used in this work. An equal amount, 0.5 wt.% of each additive (in excess of the base PMN–PT–BT composition), was incorporated by the chemical method. Each additive composition was designated using the simple notation shown in Table 1. For example, F5B5T5 corresponds to a PMN–PT–BT sample containing 0.5 wt.% Fe_2O_3, 0.5 wt.% BaO, and 0.5 wt.% TiO_2.

The details of the chemical additive method are described in [13]. Titanium isopropoxide $Ti[OCH(CH_3)_2]_4$, zinc acetate dihydrate $Zn(CH_3CO_2)_2{\cdot}2H_2O$, iron(III) acetylacetonate $Fe[CH_3COOH{=}C(O{-})CH_3]_3$, barium acetate $Ba(CH_3CO_2)_2$, and strontium acetate $Sr(CH_3CO_2)_2$ were used as raw materials for the additives. After making a 0.063 M solution of titanium isopropoxide in isopropanol, Zn acetate or Fe acetylacetonate was dissolved in the solution. While stirring the solution, a catalytic amount of nitric acid was added. For the additives containing Ba and Sr, aqueous solutions of the Ba and Sr acetate (0.033 and 0.048 M, respectively) were separately prepared and then admixed with the previous cation-containing isopropanol solution. Gelation seemed to occur immediately. The base PMN–PT–BT powders were inserted into the gel solution. The resultant slurry was stirred at <60 °C until the solvent completely evaporated. The final powders containing the chemical additives were pressed at ~80 MPa to make disk-shaped pellets. The pressed pellets were sintered at 1200 °C for 4 h in a Pb atmosphere (formed by using a calcined $PbZrO_3$ + 5 wt.% ZrO_2 powder) after burn-out of organics at 600 °C for 2 h.

The sintered samples were characterized by fired density and grain size, which were obtained by the Archimedes' principle and the linear intercept method, respectively. For electrical measurement, the sintered pellets were electroded with a silver paste after sputtering both sides of the sample with Ag–Pd. Weak-field dielectric properties of the sintered samples were measured during cooling at 2 °C/min using an LCR meter (HP4284A) at several discrete frequencies (from 10 Hz to 1 MHz) and temperatures (from 170 to −20 °C). A modified Sawyer–Tower circuit was used to observe polarization behavior with electric field. In the case of longitudinal strain measurements, a Fotonic™ Sensor (MTI 2000 Fotonic Sensor) was used. The strain and polarization measurements were conducted simultaneously at 0.1 Hz with a change in temperature from 70 to −20 °C. The apparatus for the polarization and strain measurements included a multifunction synthesizer (HP8904A),

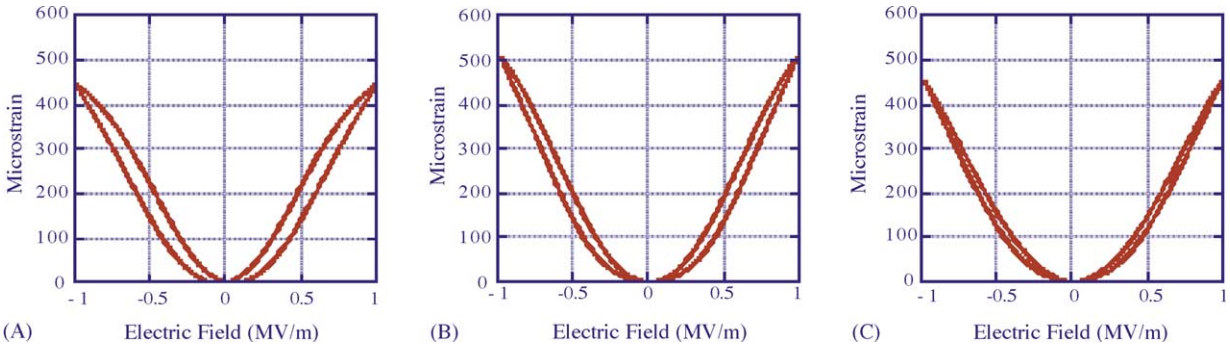

Fig. 1. Strain curves with electric field for the (A) F5B5T5, (B) B5Z5T5, and (C) S5Z5T5 samples.