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Structural and frequency dependent dielectric properties of 0.90PMN-0.10PT ferroelectrics at room temperature

Sidharth Kashyap[a*], S C Bhatt[a], Manish Uniyal[a], Gambheer Singh Kathait[b], Savita Kashyap[c] & Aditi[d]

[a]Department of Physics, H N B Garhwal University, Srinagar Garhwal – 246 174, India

[b]Department of Instrumentation Engineering (USIC), H N B Garhwal University, Srinagar Garhwal - 246 174, India

[c]Department of Education, K.L. D.A.V. P.G. College Roorkee, Uttarakhand 247 667, India

[d]Department of Zoology & Bio-Technology, H N B Garhwal University, Srinagar Garhwal - 246 174, India

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In the present study, the composition of (1-x)PMN-(x)PT for X=0.10 binary solid solution was synthesized by double step columbite precursor method with multiple heat treatments at different temperatures. XRD analysis shows the single perovskite phase with minimized pyrochlore phase. The intense peaks of XRD pattern indicates the perovskite phase of composition. It was observed that the pyrochlore phase in the material can be reduced by increase in sintering temperature and proper stoichiometry. SEM micrograph shows the polygonal, dense and compact grain boundaries. Room temperature frequency dependent nature of Dielectric constant and tangent loss of prepared composition was also measured.

Keywords: Perovskite, Pyrochlore phase, Grain boundaries, Dielectric constant, Tangent loss

Introduction

Binary solutions of Lead Magnesium Niobate and Lead Titanate are very important and well known relaxors ferroelectrics[1]. They have very high dielectric constant and super piezoelectric performance which make them ideal substances for thin film capacitor, Multi-Layer Capacitors (MLCs), actuators, biomedical tranducers and for electro-optics[2-8]. Relaxor ferroelectrics are generally ABO_3 type crystals having mixed B-Site. They have general formula $A(B_1B_2)O_3$,where B_1 is a low valence cation like Mg^{2+}, Fe^{3+}, and Zn^{2+} and B_2 is a high valence cation likeTa^{5+}, Nb^{5+9}. It was reported previously that dielectric and ferroelectric performance of relaxor ferroelectrics can be increased by proper addition of lead magnesium niobate and lead titanate[10-18]. (1-x)PMN-(x)PT is a solid solution of Lead Magnesium Niobate (PMN) and Lead Titanate(PT) i.e. $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$- $xPbTiO_3$ where x have values between 0 to 1. The properties of $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$-$xPbTiO_3$ or PMN-PT ceramics are changed as Ti concentration varies accordingly. A ceramic having low Ti content behaves as a relaxor ferroelectric and high concentration of Ti content make them a normal ferroelectric[19]. PMN-PT system gives interesting and useful dielectric and piezoelectric properties at morphotropic phase boundary (MPB)[20-22].The Morphotropic Phase Boundary (MBP) is found in the range of x=0.3 to 0.4[23,24]. The present investigation was carried out for solid solution X=0.1 or 0.90PMN-0.10PT composition and it is very close to Lead Magnesium Niobate (PMN).

It shows very high dielectric permittivity and strong piezoelectric performance, which make it an excellent material for multi-layered high density capacitors[25]. 0.90PMN–0.10PT has a diffuse phase transition temperature (T_{max}) at about 40°C and its dielectric constant at room temperature is very high (ε~10,000)[26].It is very tough task to fabricate single phase (1-x)PMN-(x)PT perovskite due to volatile nature of lead content attemperature near to its melting point. There may exists some pyrochlore phase, which reduce the dielectric and ferroelectric performance. So, to fabricate a single phase perovskite with reduced pyrochlore phase, we have implemented columbite precursor method for material preparation[27]. Therefore, some excess amount of MgO and PbO is added to starting reagent in stoichiometric proportion. It has been investigated previously that excess amount of MgO increase the dielectric and micro-structural properties with reduced pyrochlore

*Corresponding author (E-mail: sid.kashyap1@gmail.com)

phase[28,29].In the present investigation, we have prepared a solid solution of Lead Magnesium Niobate (PMN) and Lead Titanate (PT) for X=0.10 composition. The conventional solid state reaction method using columbite precursor followed by two-step sintering method was used to achieve enhanced dielectric and piezoelectric properties.

Experimental Procedures

Sample preparation

The relaxor ferroelectric material Lead Magnesium Niobate- Lead Titanate (1-x)PMN-xPT for composition X=0.10 was synthesized by two step columbite precursor method with multiple heat treatments at different temperatures. The oxides, PbO, MgO, TiO_2 and Nb_2O_5 were used as starting materials. The starting oxides were dried at 200 °C for two hr to remove moisture and other volatile impurities from the mixed sample. All the required materials were weighted in stoichiometric proportion and then grinded manually. In the primary process of sample preparation, MgO (with excess 1-2 wt%) and Nb_2O_5 were mixed properly in ethanol medium using agate mortar and pastle for 6hr and then calcined in an alumina crucible at 1110 °C for 5h. The intermediate pre-product $MgNb_2O_6$ were cooled, crushed and again mixed manually with Lead Oxide (PbO) and Titanium Oxide (TiO_2). It is very important to maintain stoichiometry of 0.90PMN-0.10PT with excess amount of MgO and PbO for useful results. Final composition 0.90PMN-0.10PT was calcined at 920 ºC for 2 h. Pellets (with 8 mm dia piston) of 0.90PMN-0.10PT were prepared under uniaxial pressure condition and then placed in closed alumina crucible and sintered twice at 1200 °C for 6 h with intermittent cooling. The calcined powder and sintered pellets of 0.90PMN-0.10PT were analyzed by X-Ray Diffraction (XRD)on an X-Pert PAN alytical diffractometer, model PW40 and the particle morphology and elemental analysis (weight %) of the ceramic were measured by scanning electron microscopy with EDAX (SEM-EDAX) using model EVO 18 Special Edition (Switzerland), manufactured by ZEISS.

XRD analysis

X-ray diffraction (XRD) method was used to identify the perovskite phases in the samples. The perovskite nature of the 0.90PMN-0.10PT ceramics was determined using an X-RAY diffractometer (XPERT-PRO) with a Cu Ka radiation source (λ =1.54059 Å), operated at a voltage of 45kV and a current of 40 mA[30].

XRD Analysis for 0.90PMN-0.10PT relaxor ferroelectrics was carried out and it shows the perovskite phase with less pyrochlore content. It gives intense peaks after double sintering process at different temperatures. Sample 0.90PMN-0.10PT was calcined at 920 °C and sintered twice at 1200 °C for 6 h with intermittent cooling and crushing. The diffraction intensity pattern of 0.90PMN-0.10PT was measured at different theta values ranging from 20° to 80° at room temperature. It is clear from the Fig. 1; all the peaks are due to perovskite phase and have rhombohedral crystal structure at room temperature. This phase structure has similarity with the data reported by B Noheda *et. al.*[31].

SEM analysis

SEM analysis of 0.90PMN-0.10PT, prepared by columbite precursor method with double sintering process was carried out. It is clear from the SEM micrographs (Fig. 2 & 3), all the grains are polygonal, compact and have sharp edge boundary[32, 33]. The average grain size of prepared sample is between ~3 µm to 7.5 µm and calculated density of pellets is between 5.8 to 6.0 gm/cm^3

EDAX analysis

Figure 4 represents the quantitative results or percent values of loss and gain of different elements

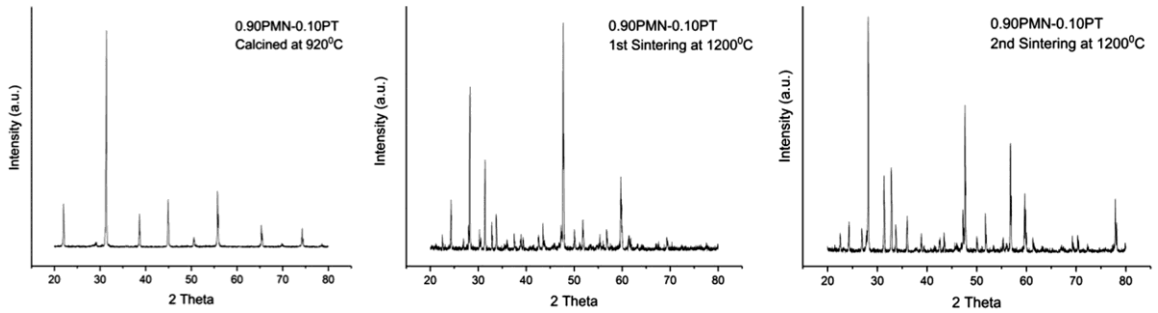

Fig. 1 — XRD patterns of the 0.90PMN-0.10PT sample calcined at 920 °C and sintered twice at 1200 °C.

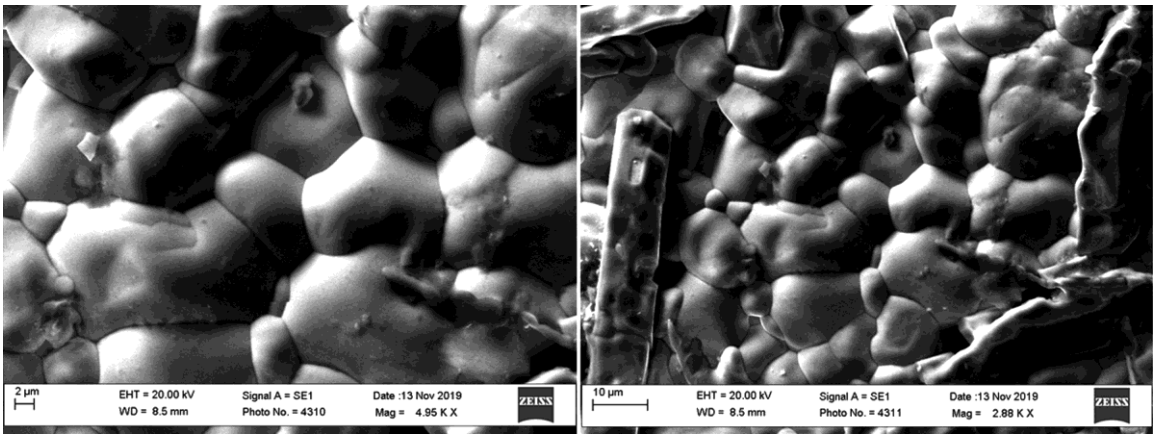

Fig. 2 — Different scale SEM Micrographs of 0.90PMN-0.10PT ceramic 1st sintered at 1200 ºC.

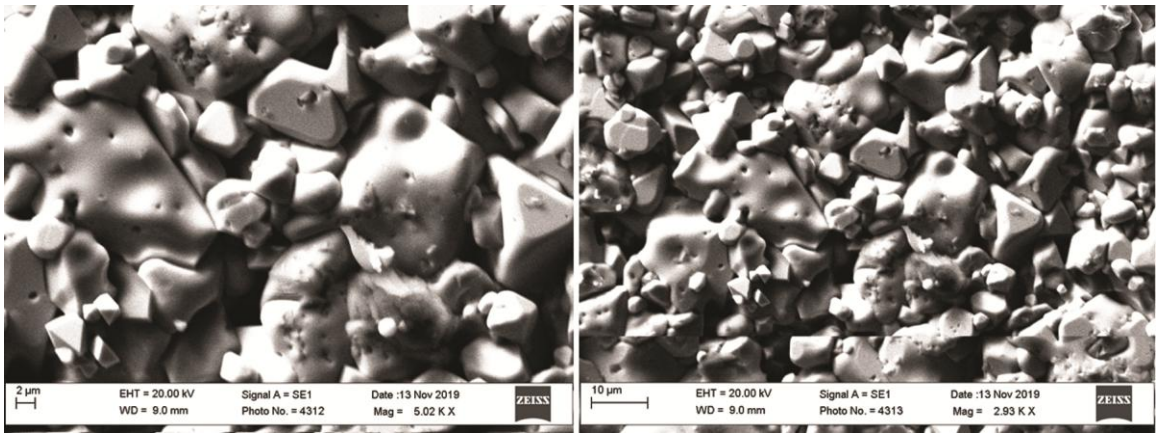

Fig. 3 — Different scale SEM Micrographs of 0.90PMN-0.10PT ceramic sintered again at 1200 ºC.

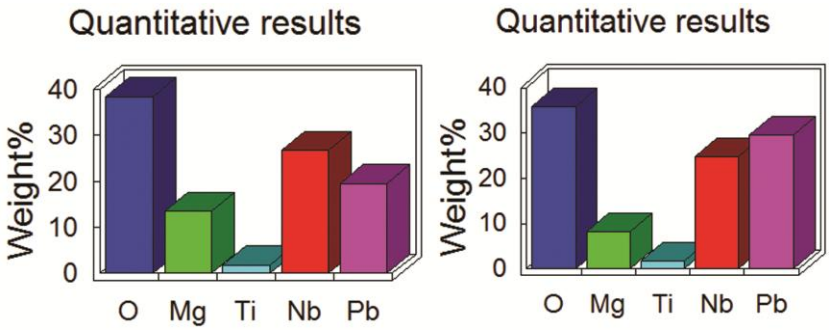

Fig. 4 — (a & b) represent the quantitative results or percent values of loss and gain of different elements of composition during the different heat treatment.

of composition during the heat treatment. It is clear from figures, O, Mg and Nbloses their weight % and some weight % of Pb and Ti contents increases after 2nd sintering process.

Dielectric Measurements

LCR meter (Fluke, PM6306) was used to measure dielectric constant, dielectric loss with the variable frequency at room temperature. Following figures (in Fig. 5) shows the frequency dependent nature of dielectric constant and tangent loss (tan δ) at room temperature. The variation of frequency was ranging between 1 KHz to 1 MHz or 1000 KHz. It is clear from the figures, the dielectric constant and loss tangent decreases as we increase frequency. This fall in dielectric constant is may be due to miss-alignment of applied electric field with the dipoles[34,35].The frequency dependence nature of electrical properties

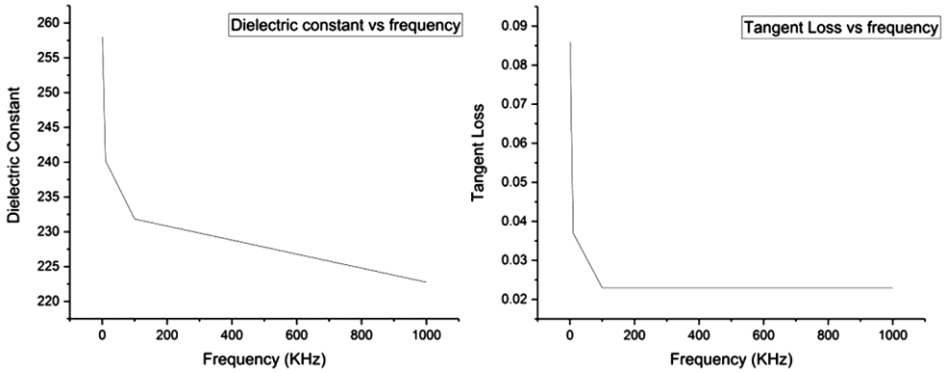

Fig. 5 — Variation of dielectric constant and loss tangent as a function of frequency at room temperature for 0.90PMN-0.10PT sample.

Table 1 — Dielectric Constant, Tangent Loss (tan δ) and Electrical Conductivity of 0.90PMN-0.10PT with different frequencies at room temperature.

Sample	Frequency (KHz)	Dielectric Constant (ε_{RT})	Loss Tangent (tan δ)	Electrical Conductivity (ohm-cm)$^{-1}$
0.90PMN-0.10PT	1	257.9894	0.086	1.23×10^{-8}
	10	240.2271	0.037	4.94×10^{-8}
	100	231.841	0.023	2.96×10^{-7}
	1000	222.7561	0.023	2.85×10^{-6}

of composition 0.90PMN-0.10PT have been plotted in graphs and also been tabulated in the following table (Table 1).

Results and Discussion

A single phase perovskite of 0.90PMN-0.10PT was synthesized by solid state reaction method via columbite route. X-Ray Diffraction graphs show the single perovskite phase of material having rhombohedral crystal structure with reduced pyrochlore phase. The pyrochlore phase can be reduced by increase in sintering temperature. The SEM micrographs show the compact and dense grains having polygonal structure. EDAX analysis of prepared sample shows the effect of sintering on the elemental weight %. The 0.90PMN-0.10PT ferroelectric shows frequency dependent dielectric response at room temperature. As we increase frequency 1KHz to 1MHz, the Dielectric Constant and Tangent Loss will also decrease due to disorder in alignment of dipoles with alternating electric field. It is also investigated that the dielectric constant is directly correlated with density of grains and sintering temperature

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