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Temperature Dependent Dielectric Properties of $PB[(MG_{1/3}NB_{2/3})_{1-X}TI_X]O_3$ for X= 0.25 Prepared By Solid State Reaction Method

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Abstract: Relaxor ferroelectric 0.75PMN-0.25PT was synthesized by two-step solid state reaction method via columbite route. The final mixed and grinded compositions was calcined at 920^{0}C for 2h and then sintered at 1200^{0}C for 6h. The XRD data show the perovskite phase of prepared material with reduced pyrochlore phase and the SEM micrographs shows the compact and dense grains. The dielectric measurement shows the temperature dependent nature having dielectric constant 13189.44 at Curie temperature (T_c).

Keywords: Relaxors, Perovskite, Calcination, Sintering, Dielectric Constant, Piezoelectric Coefficient.

Introduction

Lead based relaxor ferroelectric materials are very important materials for wide area of scientific and industrial uses. They have excellent Dielectric and Piezoelectric properties and possess a specific nature called diffused phase transition as compare to other ABO_3 type ferroelectric materials. That's why these types of materials are widely used in various applications such as multi-layer capacitors, mechanical actuators, biomedical transducers etc. (Lejeune and Boilot, 1986; Uchino, 1991). Therefore these ferroelectrics have wide scientific and industrial importance. The Lead based relaxor ferroelectrics generally have $A(B_1B_2)O_3$ type crystal structure, where B_1 is divalent or trivalent metal ion like Mg^{2+}, Ni^{2+}, Fe^{3+}, Sc^{3+} and B_2 is pentavalent metal ion like Ta^{5+}, Nb^{5+}, etc. (Sun and Cao, 2014; Luo et al. 2012). Lead Magnesium Niobate (PMN) is a well know relaxor ferroelectric material having very high value of dielectric constant (Ɛ) at its transition temperature and shows diffused phase transition (DPT) behavior. The transition temperature shifts up from -10^{0}C in pure Lead Magnesium Niobate to 40^{0}C in 0.9PMN-0.1PT, at applying electric field of frequency 100 Hz (Zhang et al. 1998). PMN-PT is a solid solution of Lead Magnesium Niobate (PMN) and Lead Titanate (PT) in stoichiometric proportion i.e. $(1-x)PbMg_{1/3}Nb_{2/3}O_3$- $xPbTiO_3$ where x exists between 0 to 1. The properties of composition $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$-

x$PbTiO_3$ are improved as Ti concentration differs in the prepared composition. Low value of Ti content behaves like a relaxor ferroelectric and as we increase the amount of Ti, the ceramic becomes a normal ferroelectric (Huang et al. 1998). PMN-PT system gives interesting and useful dielectric and piezoelectric properties at morphotropic phase boundary (MPB) (Kelly et al., 1997; Alguero et al., 2004; Kutnjak et al., 2006).The MPB boundary is found to be in the range of x=0.3 to 0.4 (Choi et al., 1989; Noblanc et al., 1993). The dielectric constant, conductivity and loss tangent of the prepared material depends on the density of the material. More dense material will be achieved by proper preparation conditions and continuous suitable high temperature sintering process. Density of this these compositions will be increased between sintered temperature range 1200^{0}C to 1300^{0}C.

It is difficult to prepare single phase (1-x)PMN-(x)PT due to volatile nature of lead content at higher temperature sintering process via solid state reaction method. There may be present some pyrochlore phase, which reduce the dielectric and piezoelectric properties. So, to reduce the pyrochole phase, we have adopted columbite precursor method for material preparation (Swartz and Shrout, 1982). So, extra amount of MgO and PbO is added to starting oxides as required. It has been reported previously that excess amount of MgO increase the electrical and structural properties (Wang, and Schulze, 1990; Kang and Yoon, 1988).

In the present study, we have prepared a mixed solid solution of Lead Magnesium Niobate PMN and Lead Titanate (PT) for x=0.25 composition. The conventional solid state reaction method using columbite precursor followed by two-step sintering method was used to achieve extraordinary and enhanced dielectric and piezoelectric properties than Lead Magnesium Niobate (PMN).

Experimental

High purity starting oxides PbO, Nb_2O_5, MgO and TiO_2 were used as starting material in stoichiometric proportion. The starting materials were dried at 150^{0}C for one hr to remove moisture and other volatile impurities. The Lead Magnesium Niobate Lead Titanate, 0.75PMN-0.25PT has been synthesized by columbite precursor method (Swartz and Shrout, 1982). In this preparation method, the stoichiometric amount of MgO and Nb_2O_5 were mixed manually in ethanol medium for 2 hr and then calcined in a closed alumina crucible at 1110^{0}C for 5 h. The intermittent pre product Magnesium Niobate, $MgNb_2O_6$ was again mixed thoroughly with Lead Oxide PbO and Titanium Oxide TiO_2 in stoichiometric proportion. Extra 8% amount of PbO was also added to starting mixture because of its volatile nature at high temperature. This excess amount of PbO will maintain Stoichiometry of the whole composition. The mixed powder (final composition) was again calcined at 920^{0}C for 2 h in closed alumina crucible. The prepared material was pelletized by using a die of diameter 8 mm and then sintered at 1200^{0}C for 6 hr.

The phase structure was measured by X-ray diffraction (XRD), on an X-Pert PANalytical diffractometer, model PW40. The XRD results indicate that only pure perovskite structure exists for 0.75PMN-0.25PT samples, obtained with two-step sintering method. The opposite faces of sintered pellets were coated with silver paste for electrical connection. The coated pellets were dried for 1 h at room temperature (25^{o}C). LCR meter (Fluke, PM6306) was used to measure dielectric constant, dielectric loss with the temperature. The LCR meter was used in conjunction with a furnace. The particle morphology and element atomic % of the ceramic were examined by scanning electron microscopy with EDAX (SEM-EDAX) using model EVO 18 Special Edition (Switzerland), manufactured by ZEISS.

Structural Analysis

XRD analysis-

X-ray diffraction method was used to investigate the crystalline properties of prepared samples. The crystalline nature of the prepared ceramics was determined using an X-RAY diffractometer (XPERT-PRO) with a Cu Ka radiation source ($\lambda =$1.54059 Å), operated at a voltage of 45 kV and a current of 40 mA (Kathait et al., 2020). The XRD patterns of pre-product $MgNb_2O_6$ and final product 0.75PMN-0.25PT are shown in the following figures. It is clear from the figures, almost all the peaks are due to perovskite phase, and reduced pyrochlore phase can be also seen. The diffraction intensity was measured from 20^0 to 80^0 for 0.75PMN-0.25PT and 20^0 to 60^0 for $MgNb_2O_6$ at room temperature. From further phase study of 0.75PMN-0.25PT, it is clear from the observed data, the prepared sample exhibits rhombohedral crystal structure at room temperature.

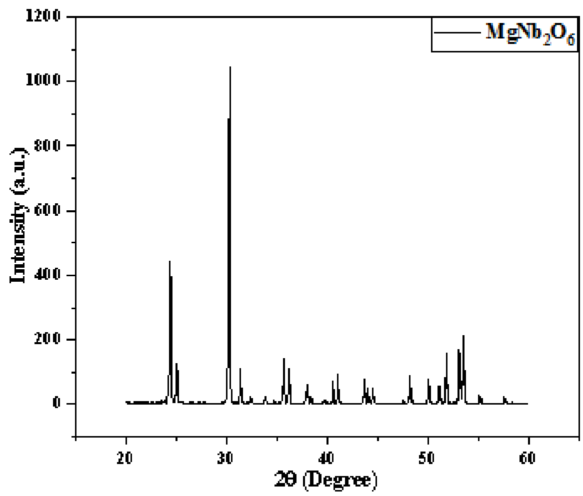

Fig 1: XRD pattern of Pre product $MgNb_2O_6$

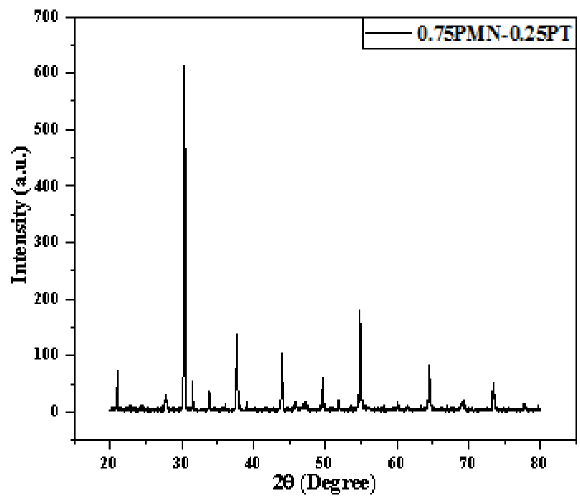

Fig 2: XRD Pattern of 0.75 PMN-0.25 PT ceramic sintered

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SEM analysis-

SEM technique was introduced to investigate the grain size and crystalline size of the prepared sample. The SEM micrographs of prepared composition 0.75PMN-0.25PT sintered at 1200^{0}C at different scale are shown in the figures. The better sintering activity like two time sintering resulted in the fast diffusion of grain boundaries, therefore eliminating pores in the microstructure. The SEM micrographs show that, grains in the prepared material are structured very close to each other that show high compactness of grains. Compact arrangement of grains is responsible for high density. Figure 3 shows the polygonal shaped grains with grain size between ~2 µm to 9.5 µm. The calculated average grain size and density of prepared sample is ~4.7 µm and 7.25 gm/cm^3 respectively. The Figure 3 indicates non homogeneity in the microstructure and had double-structure with small grain size and large grain size coexistence as found in previous study (Lejeune and Boilot, 1986).

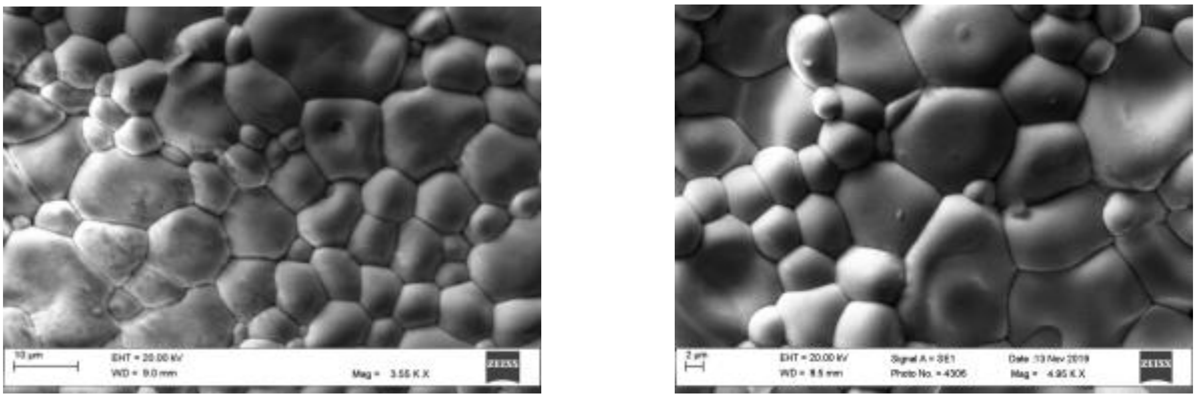

Fig 3: Different scale SEM Micrographs of 0.75 PMN-0.25PT ceramic sintered at 1200^{0}C

EDAX analysis

The table-1 and figure 4 represent the quantitative results or percent value of loss and gain of different elements of composition during the heat treatment. It has been observed that the lead escaping is significantly higher than oxygen escaping. Due to the excess of the vacancies at A-site, with respect to that at O-site, p-type conduction is expected to be present in the prepared 0.75PMN-0.25PT ceramics. If the escaping of the lead ions is high a larger number of 'holes' will be available for conduction. Therefore an increase in the A-site vacancy concentration in the samples is obtained by two-step sintering mechanism (Kathait et al., 2020).

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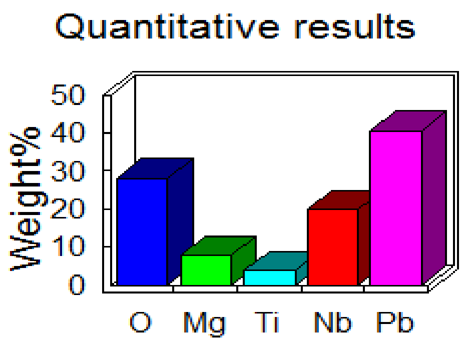

Fig 04: quantitative results of loss and gain of different elements of composition during the heat treatment

Table 1: quantitative results or percent value of loss and gain of different elements.

Elements	Weight %	Atomic %	Loss %	Gain %
O	28.06	68.59	-	9.01
Pb	40.61	7.67	11.76	-
Mg	7.66	12.33	7	-
Nb	19.98	8.41	12.1	-
Ti	3.68	3.00	16.41	-

Dielectric Properties

Figure 5 (a) and (b) shows the temperature dependent dielectric constant (Ɛ) and dielectric loss (tan(δ)) respectively of sample 0.75PMN-0.25PT for different frequencies. It is observed from figures 5(a) that composition 0.75PMN-0.25PT shows the diffuse phase transition at transition temperature (T_c) 130^0C, that's why it is called relaxer ferroelectric material. Similar to previous results the dielectric constant of prepared sample decreases with the increasing frequency. The wide nature of the dielectric constant curve near T_c, indicate the relaxer behavior of the ceramics that result in high value of piezoelectric properties. The dielectric properties of PMN–PT ceramics are greatly depend on the grain size, pores and grain-boundary. If there were many defects in ceramics, they would result in the decrease of dielectric constant and the increase of dielectric loss. Reducing the defects and grain-boundary, the dielectric properties of PMN–PT ceramics may be improved. Figure 3 indicated that the PMN–PT ceramics showed larger grain-size and grain-boundary tightness that resulted in the improved dielectric properties of the ceramics. The maximum dielectric constant at room temperature is 3517.989 for frequency 1 KHz. The transition temperature indicates the phase transition of the ceramics at 130^0C. After transition temperature, the dielectric constant decreases rapidly. The value of dielectric loss (tan(δ)) at room temperature is 0.054 and 0.121 at T_c for frequency 1KHz, which resulted from ferroelectric phase transforming to paraelectric phases. Dielectric loss follows the phase transition pattern.

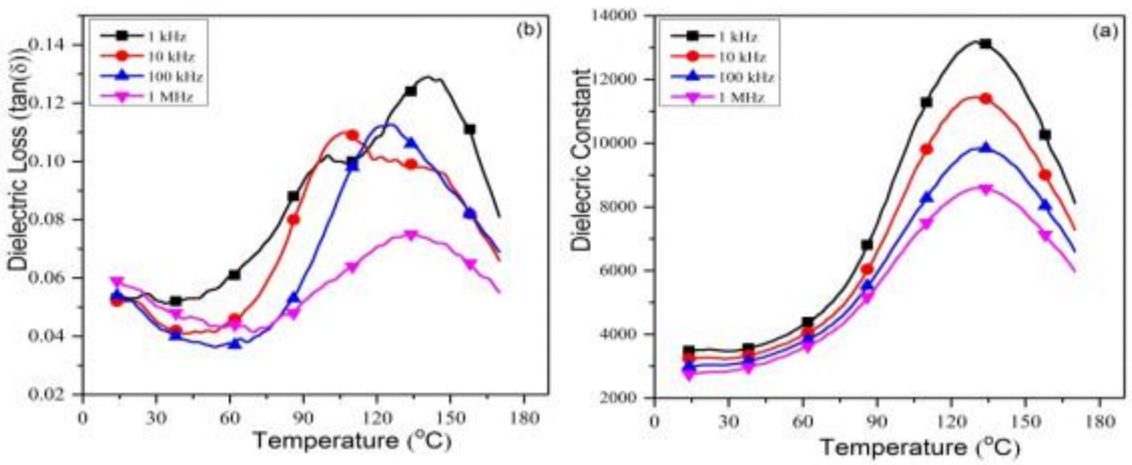

Fig 05: Dielectric properties of 0.75PMN-0.25PT (a) Dielectric constant at different temperature and frequencies. (b). Dielectric loss at different temperature and frequencies.

Conclusion

A single phase perovskite of 0.75PMN-0.25PT 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 SEM micrographs show the compact and dense grains having polygonal structure. The 0.75PMN-0.25PT ferroelectric shows the diffuse phase transition or relaxor property with temperature. The dielectric constant of 0.75PMN-0.25PT is 13189 at $T_c=130^0C$ at frequency 1 KHz.

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