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Synthesis, structural and dielectric properties of 0.8PMN–0.2PT relaxor ferroelectric ceramic

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Abstract. A 0.8PMN–0.2PT solid-solution ceramic was synthesized by columbite processing technique. The effects of sintering temperature on the density, structure and microstructure and in turn on the dielectric properties were investigated. The ceramics sintered at and above 1050°C resulted in single-phase perovskite formation. However, high density >90% is achieved only after 1170°C. Microstructural analysis revealed that grain size increases with increase in sintering temperature. A significant increase in the peak of dielectric permittivity only after 1150°C owing to increase in density is noted in this study. The quadratic law applied to this ceramic demonstrates that the transition is diffused. The broadness in phase transition and lower dielectric relaxation obtained for the composition demonstrate that the ceramic exhibits characteristics of both relaxor and normal ferroelectrics. The ceramic of composition 0.8PMN–0.2PT exhibits excellent dielectric properties $\varepsilon_{\text{r-max}} = 20294 - 27338$ at 100 Hz with $T_c = 100 - 96°C$ at low sintering temperature 1170–1180°C, respectively.

Keywords. Relaxor; dielectric properties; perovskite; pyrochlore; sintering temperature.

1. Introduction

Low-firing ceramic dielectrics exhibiting high dielectric constant with low losses are very promising in multilayer capacitors (MLCs). The low firing temperature permits the use of silver or base metals as inner electrodes instead of platinum or palladium, which reduces the cost of MLC [1]. There is a considerable interest in the lead magnesium niobate–lead titanate (PMN–PT) ceramics in MLC and actuator applications due to its high dielectric constant and high electrostatic strain of 0.1% with low hysteresis. Further, it is an attractive replacement for $BaTiO_3$ in MLC as it can be sintered at lower sintering temperature than that of $BaTiO_3$, and PZT in actuators as it exhibits high value of dielectric constant at room temperature (RT) [2–6].

It is well known that PT addition in PMN stabilizes the perovskite phase, increases the Curie temperature 'T_c' and results in improved dielectric properties [1,2,7,8,12]. Among the many compositions of PMN–PT relaxor ferroelectrics the composition 0.9PMN–0.1PT and 0.65PMN–0.35PT (MPB composition) are extensively studied [7–26]. In the synthesis of PMN and PMN–PT the formation of unwanted pyrochlore has long been recognized as a major problem [27]. Numerous attempts have been made so far to develop a processing technique to suppress the formation of undesired pyrochlore.

PMN–PT ceramics have been sintered at high sintering temperatures between 1200 and 1300°C for the formation of densified product exhibiting enhanced dielectric properties [2,9–11,21,22,24,32,33]. With increasing PT content the solid solution of PMN–PT undergoes gradual transition from relaxor to normal ferroelectric [7,8,12]. Various additives such as MgO, PbO, CuO and ZnO were used in PMN–PT system to get improved dielectric properties at lower sintering temperature [24,28–31].

Very few reports are available on the dielectric properties of the composition 0.8PMN–0.2PT [13,30–32]. In the present work, solid solution of 0.8PMN–0.2PT composition is studied systematically to analyse the effect of sintering temperature on the formation of perovskite phase, densification and microstructure to evaluate the dielectric properties and the nature of phase transition in the low sintering temperature range 1050–1180°C for its commercial applications in MLC and actuators.

2. Experimental

In the present work, ceramic of composition 0.8PMN–0.2PT is synthesized by the Swartz-suggested double-calcination route. PbO (99.9%, Sigma), MgO (99.9%, Sigma), Nb_2O_5 (99.99%, Sigma) and TiO_2 (99.99%, Sigma) are used as raw materials. In order to obtain stoichiometric composition the raw oxides are dried separately before weighing. The columbite magnesium niobate ($MgNb_2O_6$), designated as MN, is synthesized by mixing of 1.02 mol% MgO and 1 mol of Nb_2O_5. The mixture is milled in an agate mortar using acetone separately. The mixture is calcined at 1050°C

for 3 h. The dried MN, PbO and TiO_2 are weighed according to stoichiometric formula and ground well with acetone. The homogeneous mass is then calcined in an alumina crucible covered with a lid at calcination temperatures 800 and 850°C. After calcination the powder is further ground for 20 min. To this homogeneous calcined powder, polyvinyl acetate is added as a binder and the mixture is further ground for 15–20 min. Pellets of 1–2 mm thickness and 1 cm diameter are then formed by applying uniaxial pressure of 1 ton cm^{-2} in a stainless-steel die. The pellets are sintered in the closed alumina crucible at temperatures between 1050 and 1180°C for 2 h with a binder burning step at 550°C. The heating rate during calcination and sintering is 10°C min^{-1} as optimized in the previous study [11]. During the sintering the pellets were covered with the powder of the same composition to minimize the PbO losses. A detailed flowchart of the synthesis is given in figure 1.

XRD of sintered ceramics was carried out at RT (Siemens D500 diffractometer, using CuKα radiation over angular range 2θ from 10 to 100° in steps of 0.02°). XRD patterns are used to identify the structure formed and to know the relative content of the perovskite phase. The microstructure analysis is carried out using a scanning electron microscopy (SEM) analyser (JEOL JSM84A0). Grain size of the sintered ceramics is determined from the SEM micrographs using a linear intercept method. Densities of the sintered specimens are measured by the Archimedes water displacement method. For electrical measurements the surfaces of the sintered ceramic are polished using silicon carbide sand paper (220, 400 grit) to produce parallel smooth surfaces. Silver paste is coated on both surfaces of the well-polished ceramics and fired at 550°C for 30 min to provide a robust electrode. Dielectric measurements (ε_r and tan δ) are made using an impedance analyser (Model 4192A Hewlett Packard LF) in the frequency range 100 Hz–100 kHz between 30 and 170°C. The dc resistivity is measured at RT using a picoammeter (Model DPA-111). Current values are measured 2 min after application of voltage = 30 V. The characteristics and dielectric properties of the sintered ceramic are demonstrated in terms of second phase, grain size and density by analysing XRD and SEM.

3. Results and discussion

The synthesized ceramics of composition 0.8PMN–0.2PT are designated as reported in table 1. The dielectric properties ($\varepsilon_{r\text{-max}}$, T_c, ε_{rRT}, tan δ at T_c and RT) and other physical properties such as % of perovskite phase, lattice constant 'a', grain size, relative density 'D', ΔT_c (difference in $T_{c,s}$ from 100 Hz to 100 kHz), diffuseness coefficient 'δ' and electrical resistivity 'ρ' of sintered ceramics are summarized in table 2.

The XRD patterns of all ceramics (PMT1–PMT8) are presented in figure 2. The relative % of perovskite and pyrochlore phase present in sintered ceramic is calculated from the

First step — preparation of MN
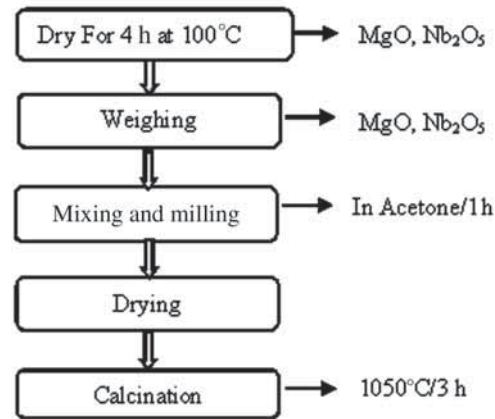
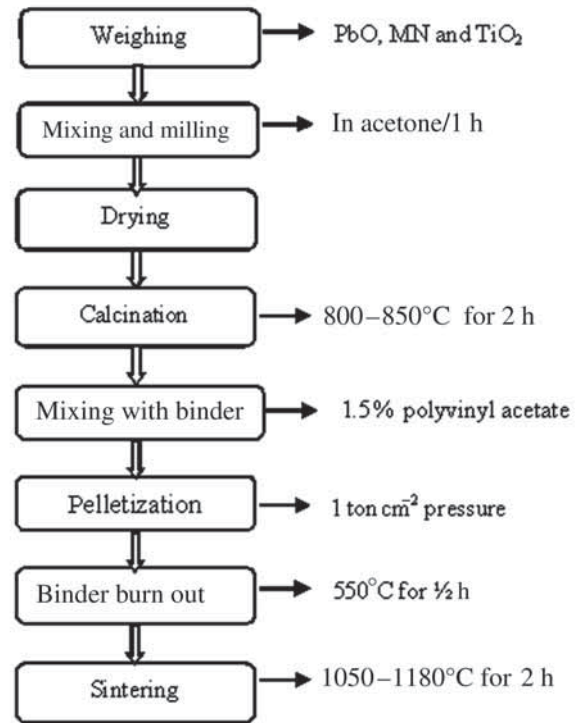**Second step — preparation of 0.8PMN–0.2PT**

Figure 1. Flowchart of material processing.

intensities of major X-ray reflection for the perovskite (110) and pyrocholre (222) phases using the following equation:

$$\text{Perovskite (\%)} = \frac{I \text{ perov} \times 100}{I \text{ perov} + I \text{ pyro}}. \tag{1}$$

In all the samples (except sample PMT5), the diffraction peaks correspond to pseudo-cubic perovskite phase (JCPDS 27-1199) and no peaks corresponding to pyrochlore phase appear, which confirms the formation of single-phase perovskite. In the sample PMT5 sintered at 1180°C, in addition to the perovskite lines, a very small diffraction peak in the region of 29° 2θ is observed, confirming the formation of pyrochlore

Table 1. Designation of sintered ceramics of composition 0.8PMN–0.2PT.

Sample	Calcination temperature (°C) and duration (h)	Sintering temperature (°C) and duration (h)
PMT1	800, 2	1050, 2
PMT2		1100, 2
PMT3		1150, 2
PMT4		1170, 2
PMT5		1180, 2
PMT6	850, 2	1050, 2
PMT7		1100, 2
PMT8		1150, 2

phase at 0.3% therein. This reflects that the decomposition of perovskite phase into pyrochlore just gets initiated at this temperature due to evaporation of PbO, similar to the earlier report [33]. The perovskite phase get stabilized in PMN–PT in the calcination temperature range 800–850°C, similar to the report by Zhao *et al* [25]. The lattice constant varies from 3.967 to 3.993 Å in case of ceramics PMT1–PMT5 calcined at 800°C. With the addition of PT, decrease of the lattice constant is observed, which is attributed to smaller ionic size of Ti (0.65 Å) ions, similar to the earlier report [18,20,32]. However, for ceramics PMT6–PMT8 calcined at 850°C the lattice constant is increased and varies from 4.08 to 4.083 Å.

The SEM micrographs of the sintered ceramics are presented in figure 3. All the ceramics exhibit similar microstructure except the variation of grain size and pore formation. The microstructure reveals increase in grain size and decrease in pore formation with increase in sintering temperature, similar to previous reports [2,10,30,32]. At lower sintering temperature, more pores are seen, beside homogeneous distribution of PMN perovskite grains. With increase in sintering temperature, pores decrease and larger variation in grain size is observed. The grain size variation is 1–2, 2–3, 2.3–3.5, 3–4.5 and 4–6 μm for samples PMT1–PMT5 sintered at 1050, 1100, 1150, 1170 and 1180°C, respectively. Grain size varies from 1–1.7 to 1.5–3.2 μm in samples PMT7 and PMT8 sintered at 1170 and 1180°C, respectively. The ceramics PMT7 and PMT8 calcined at 850°C exhibit smaller grains than ceramics PMT1–PMT5 calcined at lower calcination temperature of 800°C for the same sintering conditions.

The relative density of the samples is found to increase with increase in sintering temperature. The density of ceramics PMT1–PMT5 sintered at 800°C varies from 78 to 95% as the sintering temperature increases from 1050 to 1180°C, respectively. However, in samples PMT6–PMT8 calcined at 850°C, slightly lower density is obtained at the same sintering conditions.

The smaller grain size, slightly larger lattice constant and lower density observed at higher calcination temperature (850°C) for the same sintering conditions is due to microstructural variation resulting from compositional fluctuations, which seems to be sensitive to calcination temperature.

Table 2. Dielectric and physical properties of sintered ceramics of composition 0.8PMN–0.2PT.

Sample	$\varepsilon_{r\text{-max}}$ at 1 kHz	T_c (°C)	tan δ at T_c	ε_r at RT	tan δ at RT	Lattice constant a (Å)	Perovskite (vol%)	Grain size (μm)	D	ΔT_c (°C)	δ	ρ (Ω cm)
PMT1	9166	111	0.0642	2479	0.033	3.954	100	1–2	78	03	48	5×10^{11}
PMT2	12650	105	0.0396	2438	0.035	3.984	100	2–3	81	03	36	5×10^{11}
PMT3	14468	103	0.0406	2415	0.043	3.966	100	2.3–3.5	84	03	33	7×10^{11}
PMT4	19221	100	0.0402	2785	0.0541	3.993	100	3–4.5	87	03	31	4×10^{11}
PMT5	23549	96	0.0375	3528	0.0243	3.99	99.7	4–6	95	02	27	6×10^{11}
PMT6	8302	110	0.0524	2100	0.0416	—	—	—	77	03	38	1.2×10^{11}
PMT7	11698	107	0.034	2239	0.0317	4.083	100	1–1.7	80	02	37	2.5×10^{11}
PMT8	12923	103	0.0319	2534	0.0278	4.080	100	1.5–3.2	83	02	36	1.9×10^{11}

RT = 30°C.

The electrical resistivity of ceramics measured is $>10^{11}$ Ω cm. Resistivity of the same order was reported by Lejenue and Biolot [34].
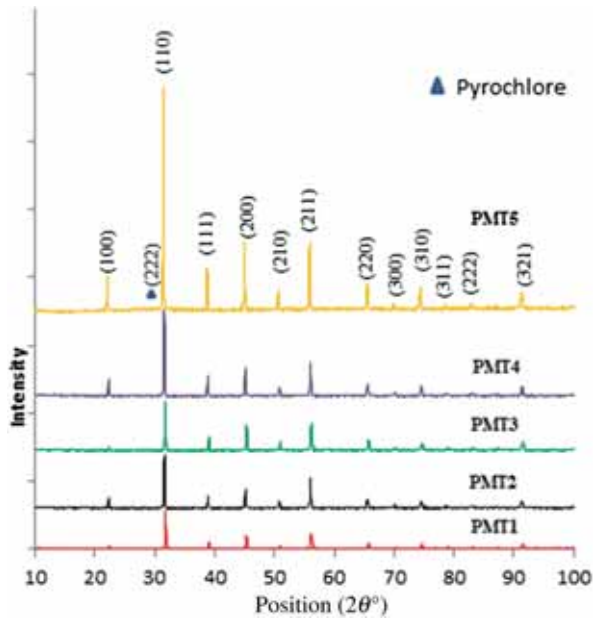

Figure 2. X-ray photographs of sintered ceramics at room temperature.

Figure 4 shows the graph of dielectric constant and the loss tangent *vs.* temperature of typical ceramics PMT2 and PMT5 at four different frequencies 100 Hz, 1 kHz, 10 kHz and 100 kHz in the temperature range 30–170°C. The peak of dielectric constant decreasing in magnitude as the frequency increases is seen in all samples, demonstrating a typical behaviour of normal or relaxor ferroelectrics. Further, the phase transition is broadened but the shift of T_c with frequency is reduced considerably. A similar trend was reported in previous studies [8,12,13,19,35]. The peak of dielectric constant increasing rapidly after sintering temperature 1150°C is observed, which seems to be due to increase in density and grain size. The dielectric constant decreases from T_c towards lower temperature, which is due to freezing of domain wall motion and its interaction with lattice defects as the temperature decreases. Increase in frequency leads to decrease in domain wall motion and therefore dielectric constant decreases with frequency, similar to the report by Garcia *et al* [21]. The transition temperature shifting to the lower side with increase in grain size is observed. A similar transition temperature shift was observed in PMN and PMN–PT systems by other researchers [2,10].

In case of a majority of ceramics the temperature of $\tan \delta_{max}$, as well as $\tan \delta_{max}$, increases with frequency. The temperature of $\tan \delta_{max}$ is lower than that of $\varepsilon_{r\text{-}max}$ at corresponding frequency, which is a typical behaviour of relaxors.
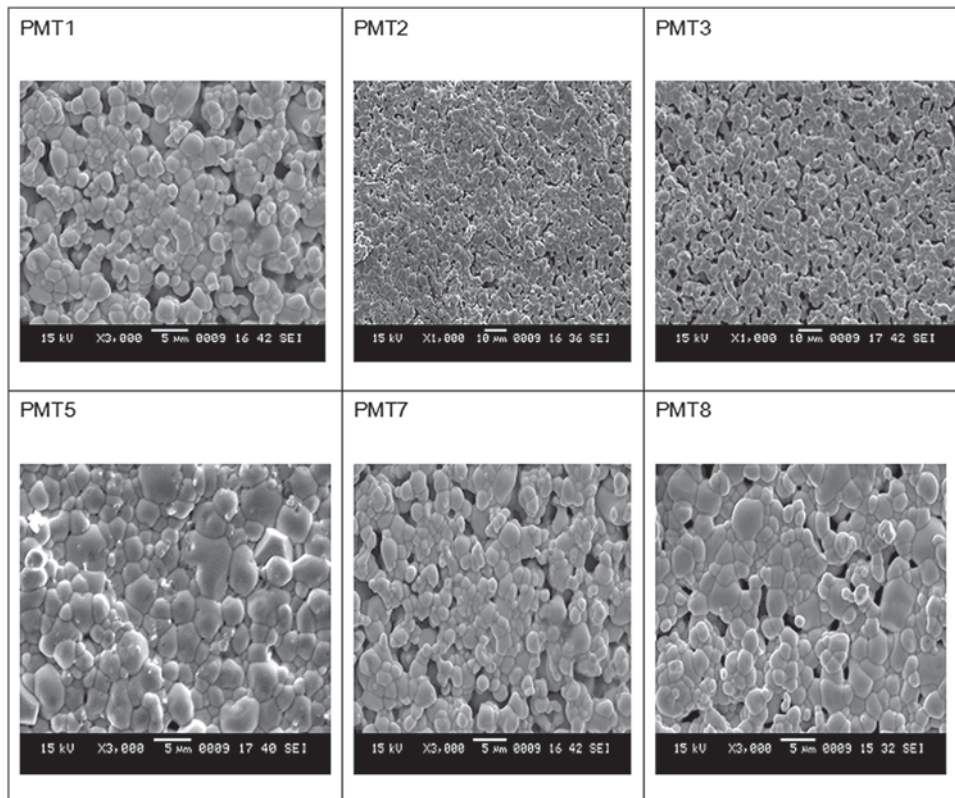

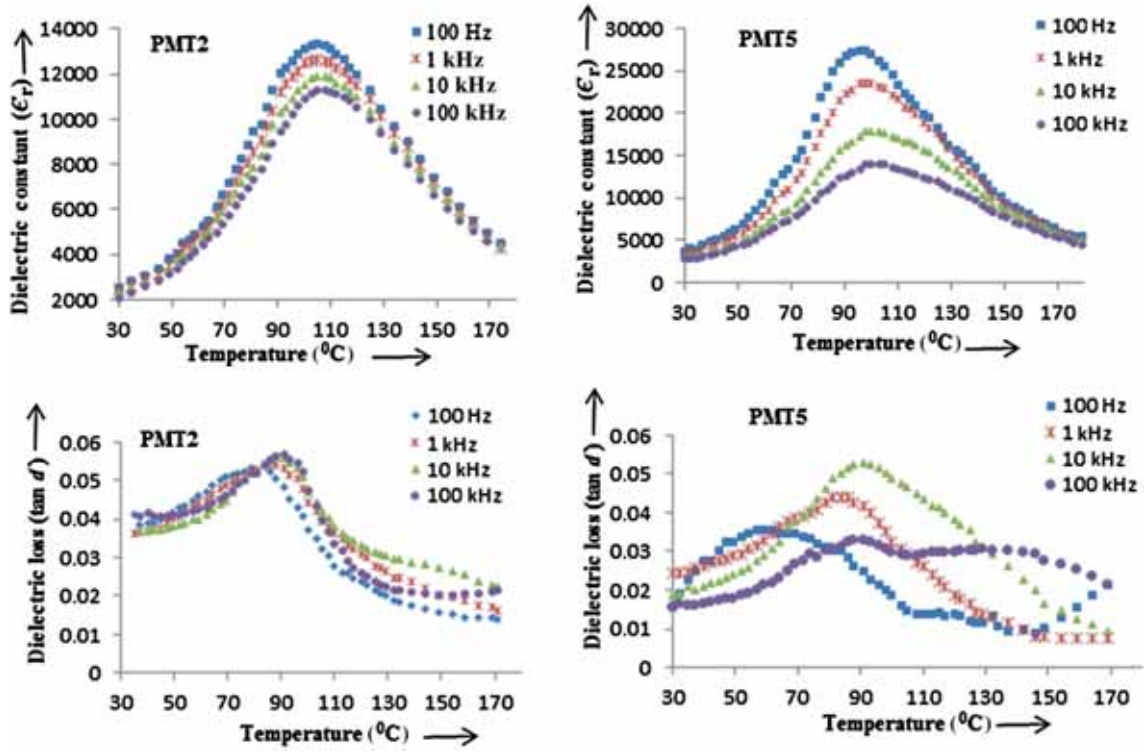**Figure 3.** Scanning electron micrographs of sintered ceramics.

Figure 4. Temperature dependence of dielectric constant and loss tangent of typical sintered ceramics at four different frequencies.

The broadened phase transition obtained is due to micropositional distribution of the B-site cations (Mg, Ti) in the PMN–PT system, which is presumably due to coexistence of Mg-rich and Ti-rich perovskite phases. The random orientation of these regions causes the structure to be macroscopically cubic but of lower symmetry in the micro-region and thus gives rise to broadened diffraction profile similar to that reported by King *et al* [5].

The lower dielectric dispersion observed for this composition can be explained in a manner similar to that of prior investigations [12]. For $T > T_m$ the polar clusters are small and do not interact. When the temperature corresponds to T_m their number and size increase. The increase in size allows interactions as the distance between two polar clusters decreases and correlation length becomes longer. Higher the correlation length L, smaller the shift of T_c with frequency. Thus the coupling of neighbouring moments implies a low-frequency relaxation as a result of interactions. The strength of interaction depends on development of polar nanoregions and then on compositions.

The following quadratic law has been used to analyse the relaxor behaviour of solid-solution ceramic 0.8PMN–0.2PT:

$$1/\varepsilon_r = 1/\varepsilon_{r\text{-max}} + (T - T_c)^2/(2\varepsilon_{r\text{-max}}\delta^2), \qquad (2)$$

where δ is called the diffuseness parameter, which is a measure of the diffuseness of transition.
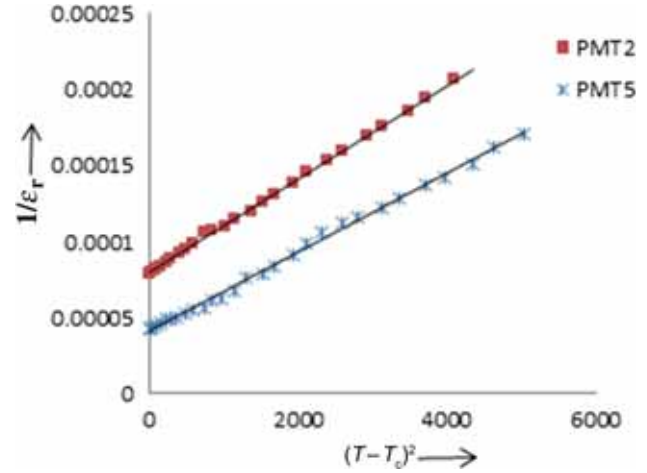

Figure 5. Quadratic graph of typical sintered ceramics.

The graph of $1/\varepsilon_r$ *vs.* $[(T - T_c)^2$ for typical samples PMT2 and PMT5 is shown in figure 5. The straight line graph demonstrates that the ceramics exhibit relaxor behaviour. The diffuseness parameter determined from the slope of graph is reported in table 2. It is observed that δ decreases as the sintering temperature increases, similar to earlier reports [2,10]. This seems to be due to enhanced micropositional fluctuations in PMN–PT ceramics as the sintering temperature increases.

Table 3. Comparison of dielectric properties of PMN–PT ceramics.

Composition	Sintering temp. (°C)	$\varepsilon_{\text{r-max}}$	T_c (°C)	Synthesis method	Reference
0.8PMN–0.2PT (PMT5)	1180	27338	96	Columbite method	Current study
0.8PMN–0.2PT	—	25000	102	Columbite method	8
0.8PMN–0.2PT	1150	24500	60	Sol combustion method	13
0.8PMN–0.2PT	1000	6500	150	Columbite method	31
0.8PMN–0.2PT	1230	18000	85	Reaction sintering method	33
0.8PMN–0.2PT with 3% excess CuO	1090, 1120	23612, 18364	86, 90	Reaction sintering method	32

Table 2 demonstrates that the dielectric constant is higher for ceramics PMT1–PMT5 calcined at 800°C than samples PMT6–PMT8 calcined at 850°C due to higher density achieved and manifestation of larger grain size at the same sintering conditions.

The maximum value of $\varepsilon_{\text{r-max}} = 27338$ and $T_c = 96°C$ at 100 Hz is obtained for ceramic PMT5 sintered at 1180°C. Addition of PT in PMN increased the transition temperature in PMN, similar to previous reports [1,7,8,12]. Decrease of the Curie temperature with sintering temperature is observed and it varies from 111 to 96 at frequency 1 kHz for ceramics PMT1–PMT5 as the sintering temperature increases from 1050 to 1180°C.

The maximum value of $\varepsilon_{\text{r-max}} = 27338$ at lower sintering temperature = 1180°C in spite of very small content of pyrochlore (= 0.3%) obtained in our study is higher than that reported earlier for this composition. The dielectric values are compared in table 3.

The maximum density = 95% reached at temperature 1180°C for PMT5 is quite high for this composition. The previous studies showed higher density for the PMN–PT system at sintering temperature greater than 1200°C [12,22]. The sintering temperature 1050–1150°C is deficient for the 0.8PMN–0.2PT ceramics to densify; therefore, relative density of the sintered ceramic is low and dielectric values are lower. With increase in sintering temperature, grain size tends to increase, porosity is gradually eliminated and microstructure becomes dense, which increase the bulk density.

Further, it is revealed in our study that the ceramic of composition 0.8PMN–0.2PT exhibits low dispersive maximum of dielectric constant with frequency, a typical behaviour between relaxor and normal ferroelectric similar to that reported by [7–9,12,19]. Sintering at low temperature = 1050°C leads to the formation of a single perovskite phase but it exhibits reduced dielectric properties owing to low density = 78%, which is further supported by SEM micrographs. However, a high-density ceramic PMT5 (density = 95%) obtained at higher sintering temperature = 1180°C resulted in significant increase in dielectric properties.

The highest value of $\varepsilon_{\text{r-max}} = 27338$ obtained for ceramic sintered at 1180°C in spite of the small content of pyrochlore shows that the dielectric properties are found to be strongly dependent on density and the grain size. However, the small content of pyrochlore is not detrimental to dielectric properties, similar to that reported by Gupta and Kulkarni [36]. Further, the study shows that calcination temperature 800°C and sintering temperature 1170–1180°C are optimized parameters to get enhanced dielectric properties.

The enhanced dielectric properties in ceramics at higher sintering temperature are attributed to high density and increased grain size of single-phase perovskite formed. Higher density indicates that larger volume fraction of ceramic is crystalline perovskite. Larger grain size provides a lower proportion of grain boundaries in the ceramics, which can be detrimental to the dielectric properties. As the grain size increases the number of grain boundaries in series decreases and dielectric constant increases [2,10,17, 31,32,36].

The high value of relative permittivity and low losses at Curie temperature exhibited by ceramic of composition 0.8PMN–0.2PT sintered at relatively lower temperature = 1170–1180°C show that it is a potential candidate in MLCs and actuators.

4. Conclusion

Enhanced dielectric properties are obtained for ceramics calcined at 800°C and sintered at 1170–1180°C owing to single-phase formation, high density and large grain size.

The composition 0.8PMN–0.2PT exhibited a broad transition, which is less dependent on frequency; hence, it demonstrated a mixed behaviour between relaxor and normal.

The ceramic of composition 0.8PMN–0.2PT attained large $\varepsilon_r = 27338$ and diffuse maximum of dielectric constant. The lowest loss at low sintering temperature = 1180°C shows that it is a promising candidate for use in MLCs and actuators.

The relative density and grain size increase with sintering temperature and thus lead to increase in dielectric constant, as revealed. The dielectric properties are found to be strongly dependent on density and the grain size. However the small content of pyrochlore does not dilute the dielectric properties seriously, as revealed in this study.

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