Journal of the European Ceramic Society 20 (2000) 2029–2034

Preparation and characterisation of $Pb(Fe_{1/2}Ta_{1/2})O_3$ relaxor ferroelectric

W.Z. Zhu *, A. Kholkin, P.Q. Mantas, J.L. Baptista

Department of Ceramic and Glass Engineering,UIMC, University of Aveiro, 3810 Aveiro, Portugal

Received 16 August 1999; received in revised form 29 February 2000; accepted 12 March 2000

Abstract

The reaction sequences between the oxides at various calcining temperatures were examined through the identification of the reaction products. Formation of pyrochlore phase with tetragonal symmetry is a required preparatory step for subsequent generation of perovskite phase. Most of the pyrochlore phase turns into the perovskite phase in the temperature range of 700–800°C and this conversion persists up to 950°C. The double calcination approach seems infeasible in promoting the pyrochlore to perovskite transformation in the presence of excess lead oxide since the decomposition of the pyrochlore phase is a rather sluggish process. Sintered $Pb(Fe_{1/2}Ta_{1/2})O_3$ displays ferroelectric relaxor behavior whose relative permittivity maximum exhibits high value ($\varepsilon'_{max} = 17\ 500$ at 248 K at 100 Hz). The distinct relaxor behaviour along with the further enhanced permittivity values for the annealed specimen reveal that the annealing treatment is mainly characterized by the elimination of the pyrochlore phase rather than the formation of the ordering in the B-site cations. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Ferroelectric properties; $Pb(Fe,Ta)O_3$; Perovskite; Reaction sequence

1. Introduction

Lead-based compounds with the general formula of $Pb(B^{I}_{x}B^{II}_{1-x})O_3$ and partially ordered perovskite structures normally exhibit ferroelectric relaxor behaviour in the weak-field dielectric response.[1–4] They are characterised by a diffused phase transition (DPT) and frequency-dependence of the temperature of the dielectric permittivity maximum (T_m). Due to their excellent dielectric, ferroelectric, and electrostrictive properties, these relaxor ferroelectrics are receiving increasing attention, and as a result, many investigations have been carried out on the preparation, characterisation, and applications of these materials.[5–7] However, the overwhelming majority of studies up to now have been done on the niobate compounds with comparatively little attention to their tantalate counterparts.

Preparation of lead-based ferroelectric relaxors with perovskite structures still remains a challenging task, since it inevitably involves the formation of parasite pyrochlore-type phase. The difficulties by which the perovskite phase can be fabricated have been assessed by Shrout et al.[8] from both kinetic and thermodynamic point of view. For some complex relaxor compounds, ceramic processes that improve the reactivity of raw materials, especially that of the B-site cation oxides, such as a better milling/mixing procedure and a process in which the PbO volatility is inhibited, allow the formation of the perovskite structure. The columbite precursor method,[9] in which the more refractory B-site cations are reacted prior to the reaction with PbO, and thereby bypassing the reaction sequence for the formation of the pyrochlore phase, is very effective in the fabrication of stoichiometric perovskite relaxors. The only drawback of this approach is its added complexity and ensuing high cost to the processing. For other lead-based relaxor compounds which have considerably lower electronegativity differences and tolerance factors, perovskite phases are difficult to synthesize because of the thermodynamic limitation. Increasing the tolerance factors and electronegativity differences of such compounds by the addition of $BaTiO_3$ or $SrTiO_3$, is found highly successful in stabilizing the perovskite structure.[10]

The synthesis of the perovskite $Pb(Fe_{1/2}Ta_{1/2})O_3$ (PFT) is scarcely reported compared with its niobate analogue $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN). The only paper[11] dealing with the processing of $Pb(B^{I}_{x}B^{II}_{1-x})O_3$-type compounds pointed out that the maximum volume fraction of the perovskite

---

* Corresponding author.

PII: S0955-2219(00)00094-7

phase is 0.86 in PFT versus 0.97 in PFN, when powders are calcined at 900°C, and suggested that Nb is favoured over Ta for the sake of perovskite formation.

In the present study, the reaction sequences during the calcination of PFT at different temperatures were examined with the aid of the X-ray diffraction (XRD). Double calcination approach was attempted to compare with the results of one-step calcination. The weak-field dielectric response was given for the sintered polycrystalline PFT ceramic body.

2. Experimental procedure

High purity Ta_2O_5 (99.99%), Fe_2O_3 (>99.5%), and $PbCO_3$ (>99%) were weighed in the stoichiometric ratio, together with 10 wt.% excess of $PbCO_3$ for lead loss compensation. The mixture was ball-milled in alcohol, in a polyethylene container, for 12 h, using yttria-stabilized zirconia balls. Dried powders were ground again by pestle in an agate mortar for several minutes, to break up some agglomerates. Lots of approximately 10 g of the mixture were calcined in air at selected temperatures, between 600 and 950°C, in covered alumina crucibles. The calcined product was ball-milled again for 6 h in the same manner as described before for the breaking up of the soft agglomerates. Powders were sieved at 45 μm. For sintering, pellets of 10 mm diameter and around 2 mm thick were uniaxially pressed at 100 MPa, followed by cold isostatic pressing at 300 MPa. The firing was carried out at 1050°C for 1 h with a heating and a cooling rate of 15°C/min. An inverted crucible configuration was adopted to prevent the lead loss.

X-ray diffraction (XRD) analysis was performed on calcined and fired powders using CuK_α radiation and a scanning speed of 1°/min.

Samples for the dielectric measurements were prepared by polishing the parallel surfaces of pellets with fine alumina sand papers, followed by sputtering gold electrodes and applying air-dried silver paint to ensure good electric contact. Dielectric measurements were carried out on an automated system, whereby a digital temperature controller (model 9650) and a Solartron 1260 impedance/Gain-Phase Analyser controlled by a desk-top computer were employed. Dielectric permittivities and dissipation factors were acquired at various frequencies, between 100 Hz and 1 MHz, as the samples were heated at a rate of 1°C/min from 150 to 300 K, a temperature range where it is observed a peak of the dielectric permittivity.

3. Results and discussion

Like other PbO-based binary system, the reaction sequences between PbO and Ta_2O_5 depend on the reactivity in each batch of raw material. In this work, emphasis is focused on the preparation of single perovskite phase PFT through direct reaction technique and on the related reaction mechanism.

3.1. Calcination of $4PbCO_3/Fe_2O_3/Ta_2O_5$

Fig. 1 illustrates the XRD profiles of products obtained at different calcining temperatures. When the mixture is calcined at 600°C, peaks of $FeTaO_4$, PbO and pyrochlore phase Pb_3FeTaO_7 can be indexed, according to the standard JCPDS cards. Neither $Pb_3Ta_4O_{13}$, a cubic pyrochlore phase which is supposed to form at the early stage of reaction,[8] nor $Pb_2Ta_2O_7$, a rhombohedral pyrochlore phase which is normally the reaction product of $Pb_3Ta_4O_{13}$ with PbO,[8] was detected in the present investigation. Additionally, no peak of the $Pb_2Fe_2O_5$ phase was found. The absence of these phases indicates that there is no preferred reaction of PbO with Fe_2O_3 or Ta_2O_5. Pb_3FeTaO_7 is considered to be isostructural to $Pb_3Ta_2O_8$ where Fe and Ta ions share common B-sites, and oxygen vacancies are supposed to be created to keep electrical neutrality. Pb_3FeTaO_7 is a distorted pyrochlore with a tetragonal symmetry similar to that of

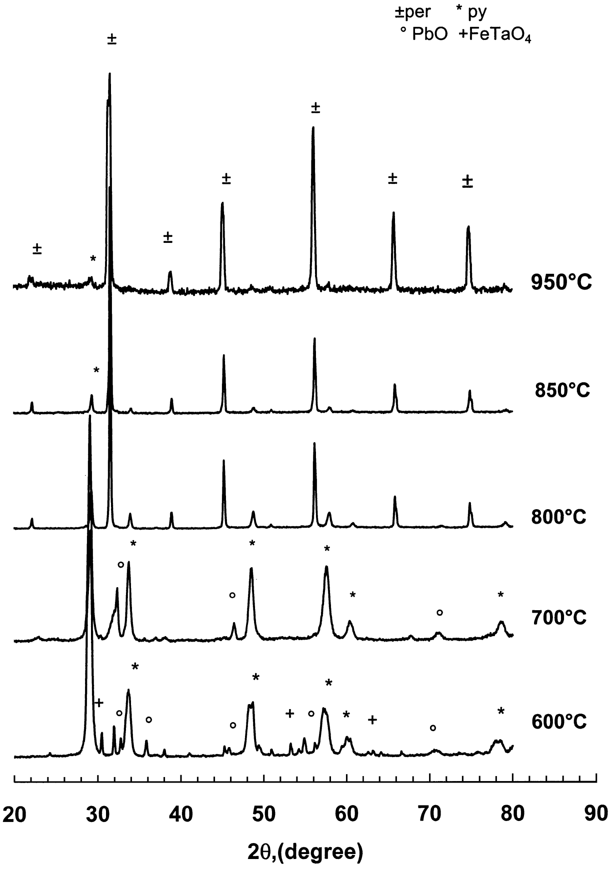

Fig. 1. XRD patterns of mixture of $4PbO/Fe_2O_3/Ta_2O_5$ calcined at different temperatures. The peaks of the pervoskite and pyrochlore phases are marked by ±per and *py, respectively.

the $Pb_3Nb_2O_8$ phase.[8] The reaction sequences in the mixture at 600°C is thought to be:

$$PbCO_3 \rightarrow PbO + CO_2 \uparrow \tag{1}$$

$$Fe_2O_3 + Ta_2O_5 \rightarrow 2FeTaO_4 \tag{2}$$

$$3PbO + FeTaO_4 \rightarrow Pb_3FeTaO_7 \tag{3}$$

It seems that the dominating reaction is formula (2) reaction. But we have not any experimental evidence to say so. The overall reaction of $4PbCO_3/Fe_2O_3/Ta_2O_5$ calcined at 600°C is:

$$\begin{aligned}4PbCO_3 + Fe_2O_3 + Ta_2O_5 \rightarrow\ & PbO + FeTaO_4 \\ & + Pb_3FeTaO_7 + 4CO_2 \uparrow\end{aligned} \tag{4}$$

As can be seen in Fig. 1, only PbO and the pyrochlore phases are detected at 700°C. It can also be noted that the intensities of the pyrochlore peaks increase at the expense of those of the $FeTaO_4$ phase, indicating that reaction (3) proceeded at a faster speed, and is probably completed at this temperature. The perovskite phase is not yet discernable at this temperature.

At 800°C, peaks of the cubic perovskite PFT phase appear accompanied by a sharp decrease in the intensities of the peaks of the pyrochlore phase and PbO. For powders where only the perovskite and the pyrochlore phases are detected, the relative amount of each phase can be readily determined by measuring the intensity of the strongest XRD peaks. For example, the volume fraction of the perovskite phase can be calculated by[9]

$$\mathrm{Per}\% = \frac{I_{(110)\mathrm{per}}}{I_{(110)\mathrm{per}} + I_{(220)\mathrm{py}}} = \times 100\% \tag{5}$$

where $I_{(110)\mathrm{per}}$ and $I_{(220)\mathrm{py}}$ refers to the relative intensity of the (110) and (220) planes of the perovskite and pyrochlore phase, respectively.

The relative amount of the perovskite PFT is shown in Table 1. As expected it increases with increasing the calcination temperature, but it is still not complete at 950°C, the highest calcination temperature. This is probably due to the fact that an excess of PbO is present in the system.

Table 1
Relative amount of the perovskite phase of the initial $4PbCO_3/Fe_2O_3/Ta_2O_5$ mixture at different calcination temperatures and calcination procedures. The amounts are in volume fraction

Single calcination			Double calcination	
800°C	850°C	950°C	800/850°C	800/950°C
85.2%	93.7%	95.4%	87.3%	94.7%

3.2. Double calcining at 800/850°C and 800/950°C

The results of the first calcination seem to indicate that the formation of the pyrochlore phase is an inevitable route leading up to the generation of the perovskite phase. Most of the pyrochlore phase turns into perovskite structure in a narrow temperature range, 700–800°C, with the remaining part transforming gradually to perovskite as the calcining temperature is further increased. Therefore, it could be concluded that the nucleation of the perovskite takes place in the pyrochlore phase. In the preparation of PFN ceramics, Fu et al.[5] introduced the double calcination approach to obtain a pure perovskite phase. The authors claimed that the nucleation of PFN was accelerated by the appearance of an intermediate phase. In an anticipation of a further reducing amount of the deleterious pyrochlore phase at lower calcining temperature, the double calcination technique was employed here. Products calcined at 800°C were ball-milled again, dried and calcined at 850 and 950°C, respectively. XRD patterns are shown in Fig. 2 and the corresponding relative fraction of perovskite phase is also listed in Table 1. It is noteworthy that the conversion of the pyrochlore to the perovskite slows down during the second calcination, as evidenced by the decreasing fraction of the perovskite phase when one compares the results of double calcination at 800/850°C with those of single calcination at 800°C (Table 1). A comparable amount of the perovskite phase to that of single calcination at 950°C was only achieved at 800/950°C. Therefore, the second calcination procedure is not effective in promoting the complete formation of the perovskite phase.

The experimental results of the calcination show that $FeTaO_4$ is readily formed in the beginning of the heating process [Eq. (2)], and that the solid state reaction proceeds with the incorporation of PbO in this phase. The perovskite phase appears through the formation of an intermediate phase, the Pb_3FeTaO_7 pyrochlore phase, by the reaction

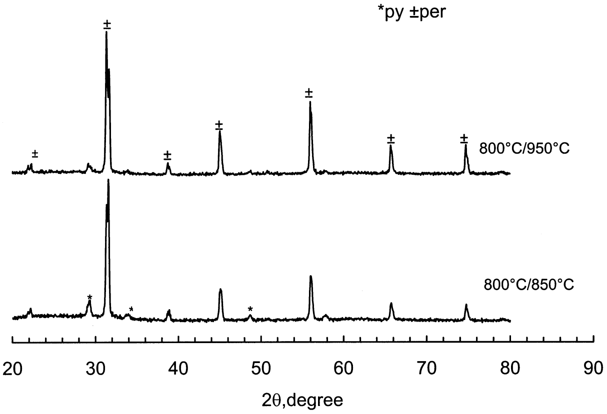

Fig. 2. XRD profiles of double-calcined products.

$$Pb_3FeTaO_7 \rightarrow 2Pb(Fe_{1/2}Ta_{1/2})O_3 + PbO \qquad (6)$$

Because we used an excess of PbO in order to prevent its loss at higher temperatures, reaction (6) is hindered by its presence, and even at 950°C the reaction is not complete. Therefore, using this procedure we probably arrive to the situation where the ordering in the B-site cations is not achieved due to the decomposition proposed by reaction (6). The electrical measurements should clarify this point.

3.3. Dielectric properties of polycrystalline PFT ceramics

3.3.1. Sintering characteristics

Fig. 3 gives the XRD profile of PFT ceramics sintered at 1050°C for 1 h in PbO-rich atmosphere using powders of the single calcination at 850°C. Parameters related to the sintering characteristics are listed in Table 2. Nearly pure perovskite PFT ceramics with high density and low weight loss were fabricated. The lattice parameter calculated using least-square method in which all the peaks of the cubic perovskite phase within the scanned interval were included, is consistent with a previously reported value.[11] A theoretical density of 9.60 g/cm^3, which is comparable to that in the literature,[11] was calculated, and the sintered specimen had a relative density of 96%. The densification was presumably promoted through liquid-phase sintering due to the presence of the PbO excess. In addition, the inverted crucible approach together with the compensating atmosphere prevents lead loss. The amount of the perovskite phase increased a little compared with the calcination value at 950°C, showing that the pyrochlore phase is still stable at sintering temperature.

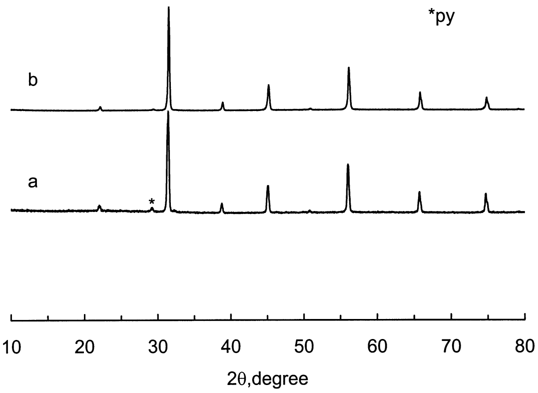

Fig. 3. XRD profiles of the (a) as-sintered polycrystalline PFT ceramics and (b) the sintered sample followed by annealing at 900°C for 24 h.

Table 2
Sintering characteristics of PFT ceramics sintered at 1050°C

Lattice parameter	Density	Weight loss	Shrinkage	Perovskite phase
a=4.015 A°	9.19 g/cm^3	3.5%	33.6%	96.8%

3.3.2. Dielectric response

Fig. 4 shows data for the real and the imaginary parts of the relative permittivity from the PFT ceramics over a range of temperature in the frequency range of 100 Hz to 1 MHz. It turns out that the permittivity maximum is diffused and slighted frequency-dependent. A permittivity maximum of 17 500 was observed at 248 K (Table 3), which is remarkably higher than the previously reported value (3700).[12] This behaviour is most probably related to the disordered state in the B-site cations due to the type of procedure used, as anticipated in the previous Section 3.2. The dielectric response of the sample annealed at 900°C for 24 h is presented in Fig. 5. Even after prolonged heat-treatment at elevated temperature, the typical relaxor behaviour, namely, the upward shift of the temperature of the permittivity maximum with increasing frequency and slight frequency-dependence of the permittivity values below the Curie temperature, indicate that the annealed specimen is still in the disordered state. Furthermore, the significantly enhanced permittivity values (Table 4) as

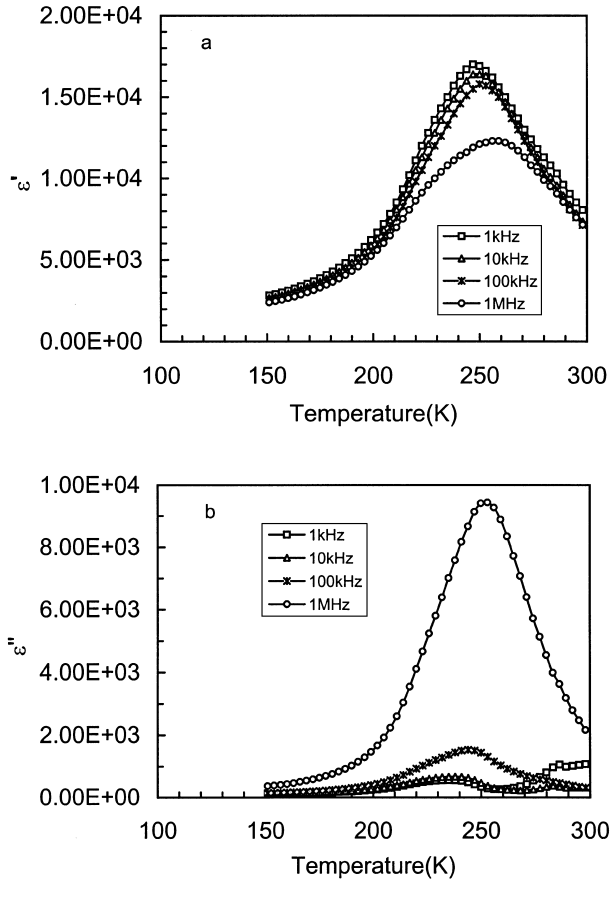

Fig. 4. Variation of (a) real, and (b) imaginary parts of the relative dielectric permittivity as a function of temperature at different frequencies, of the sample sintered at 1050°C.

Table 3
Dielectric properties of polycrystalline PFT ceramics sintered at 1050°C

Frequency	ε'		ε''	
	Maximum	Temperature (K)	Maximum	Temperature (K)
100 Hz	17 500	248	559	235
1 kHz	17 000	249	559	238
10 kHz	16 400	250	673	238
100 kHz	15 800	252	1530	245
1 MHz	12 300	256	9440	253

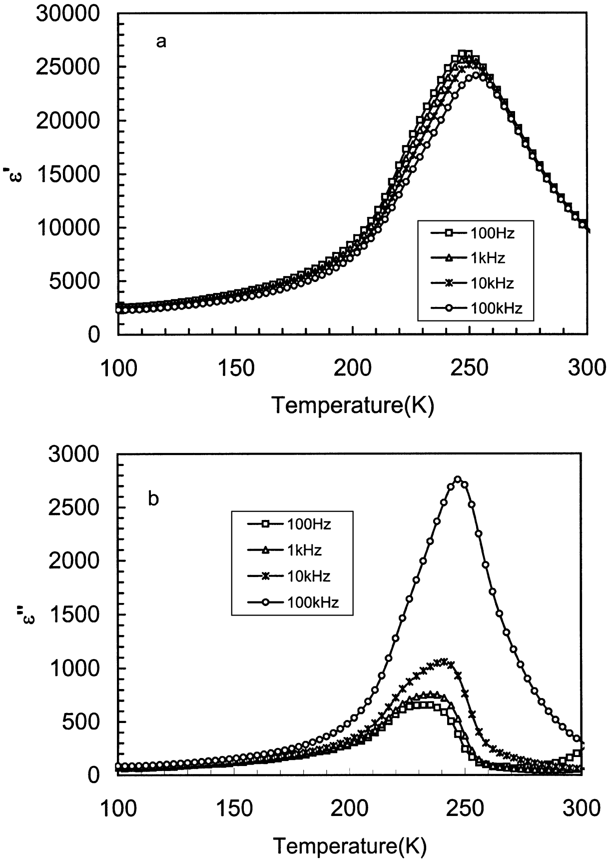

Fig. 5. Variation of (a) real, and (b) imaginary parts of the relative dielectric permittivity as a function of temperature at different frequencies, of the sample annealed at 900°C for 24 h.

compared to those of the fresh sample can be attributed to the nearly elimination of the secondary pyrochlore phase (within the limit of XRD detection) as also confirmed by XRD results shown in Fig. 3, and therefore, the annealing treatment performed in the present study is supposed to be dominated by the decomposition of the pyrochlore phase represented by the reaction (6) instead of ordering process between B-site cations as normally expected for $Pb(B'_{1/2}B''_{1/2})O_3$-type relaxor ferroelectrics,[13] which has already been predicated in the preceding section.

Table 4
Dielectric properties of the PFT sample annealed at 900°C for 24 h

Frequency	ε'		ε''	
	Maximum	Temperature (K)	Maximum	Temperature (K)
100 Hz	26 171	247	655	235
1 kHz	25 747	250	756	235
10 kHz	25 112	250	1055	241
100 kHz	24 135	253	2756	247

4. Conclusions

(1) In the conventional direct reaction approach, formation of the pyrochlore phase with tetragonal symmetry is an indispensable route for subsequent generation of PFT perovskite phase. Double calcination is ineffective in minimizing the pyrochlore phase since the decomposition of the pyrochlore phase is retarded by the presence of the excess lead oxide.

(2) Sintered $Pb(Fe_{1/2}Ta_{1/2})O_3$ is a relaxor ferroelectric whose permittivity maximum can reach as high as 17 500 at 248 K at 100 Hz, the sample annealed at 900°C for 24 h still shows typical relaxor behaviour with further improved dielectric properties due to the elimination of the pyrochlore phase.

Acknowledgements

One of authors (W.Z. Zhu) is grateful to the Foundation for Science and Technology (FCT) of Portugal (PRAXIS XXI/BPD/16300/98) for its financial support during his stay in Portugal.

References

1. Swartz, S. L., Shrout, T. R., Schulze, W. A. and Cross, L. E., Dielectric properties of lead-magnesium niobate ceramics. *J. Am. Ceram. Soc.*, 1984, **67**, 311–315.
2. Mulvihill, M. L., Cross, L. E., Cao, W. W. and Uchino, K., Domain-related phase transition like behaviour in lead zinc niobate relaxor ferroelectric single crystals. *J. Am. Ceram. Soc.*, 1997, **80**, 1462–1468.
3. Akbas, M. A. and Davies, P. K., Processing and characterization of lead magnesium tantalate ceramics. *J. Mater. Res.*, 1997, **12**, 2617–2622.
4. Robert, G., Demartin, M. and Damjanovic, D., Phase diagram for the $0.4Pb(Ni_{1/3}Nb_{2/3})O_3$-$0.6Pb(Zr,Ti)O_3$ solid solution in the vicinity of a morphotropic phase boundary. *J. Am. Ceram. Soc.*, 1998, **81**, 749–753.
5. Fu, S. L. and Chen, G. F., Fabrication of perovskite $Pb(Fe_{1/2}Nb_{1/2})$ and reaction mechanism. *Ferroelect.*, 1988, **82**, 119–126.
6. Bouquin, O., Martine, L. and Boilot, J. P., Formation of the perovskite phase in the $PbMg_{1/3}Nb_{2/3}O_3$-$PbTiO_3$ system. *J. Am. Ceram. Soc.*, 1991, **74**, 1152–1156.

7. Sekar, M. M. A., Halliyal, A. and Patil, K. C., Syntheis, characterization, and properties of lead-based relaxor ferroelectrics. *J. Mater. Res.*, 1996, **11**, 1210–1218.
8. Shrout, T. R. and Halliyal, A., Preparation of lead-based ferroelectric relaxors for capacitors. *Am. Ceram. Soc. Bull.*, 1987, **66**, 704–711.
9. Swartz, S. L. and Shrout, T. R., Fabrication of perovskite lead magnesium niobate. *Mater. Res. Bull*, 1982, **17**, 1245–1250.
10. Halliyal, A., Kumar, U. and Newnham, R. E., Stabilization of the perovskite phase and dielectric properties of ceramics in the $Pb(Zn_{1/3}Nb_{2/3})O_3$-$BaTiO_3$ system. *Am. Ceram. Soc. Bull.*, 1987, **66**, 671–676.
11. Ling, H. C., Yan, M. F. and Rhods, W. W., Phase stability in $Pb(B'^{3+}_{1/2}B''^{5+}_{1/2})O_3$ and $Pb(B'^{2+}_{1/3}B''^{5+}_{2/3})O_3$ compositions. *Ferroelectr.*, 1989, **89**, 69–80.
12. Yamashita, Y. and Ichinose, N., Can relaxor piezoelectric materials outperform PZT(Review), ISAF'96, *Proc. of the 14 IEEE Int. Symp. Appl. Ferroelectr.*, 10th, 1996, **1**, 71–77.
13. Chu, F. and Setter, N., The spontaneous relaxor-ferroelectric transition of $Pb(Sc_{05}Ta_{0.5})O_3$. *J. Appl. Phys.*, 1993, **74**, 5129–5134.