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Mechanical activation synthesis and dielectric properties of 0.48PFN–0.36PFW–0.16PZN from mixed oxides

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Abstract

Nanocrystalline 0.48PFN–0.36PFW–0.16PZN phase of perovskite structure was successfully prepared via mechanical activation of mixed oxides of PbO, Fe₂O₃, WO₃, Nb₂O₅ and ZnO for more than 15 h at room temperature. The powder derived from 20 h of mechanical activation exhibits a particle size in the range of 10–20 nm. It undergoes decomposition upon heat treatment to pyrochlore phase before a single perovskite phase was developed at the sintering temperature of 820°C for 45 min. The sintered ceramic exhibits a density of ~98% theoretical density and a maximum dielectric permittivity of ~9357 at the Curie temperature of ~27°C measured at a frequency of 100 Hz. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: 0.48PFN–0.36PFW–0.16PZN; Mechanical activation; Dielectric properties; XRD

1. Introduction

The solid solutions of Pb(Fe_{1/2}Nb_{1/2})O₃–Pb(Fe_{2/3}W_{1/3})O₃–Pb(Zn_{1/3}Nb_{2/3})O₃ (abbreviated as PFN–PFW–PZN) of perovskite structure have been recognized as suitable materials for multilayer ceramic capacitors because of their low firing temperatures below 900°C, high dielectric constants and low dielectric losses [1,2]. Yonezawa [1,3] investigated widely into these compositions and reported that the composition of 0.48PFN–0.36PFW–0.16PZN exhibited many of the most desirable properties required for a number of applications. It was subsequently employed as dielectrics in multilayer ceramic capacitors [4].

Unlike the synthesis of many other lead-based relaxor ferroelectrics whereby several processing routes have been explored, previous studies made on this ternary system were based on the conventional ceramic processing route [1,2,5–7]. The five constituent oxides are mixed in a ball mill, calcined at around 750°C, before the powder compacts were subjected to sintering at ~850°C, resulting in either a single perovskite phase or a mixture of perovskite and pyrochlore phases [2,5,8,9]. Furthermore, varying amounts of other secondary phases, such as lead tungstate (Pb₂WO₆) and zinc ferrite (ZnFe₂O₄), were also detected

when sintering is carried out at above 800°C for 1 h [2]. The formation of these secondary phases was attributed to the preferential reactions between the oxides involved [2]. Natarajan and Dougherty [5] reported recently that the maximum dielectric permittivity of 0.48PFN–0.36PFW–0.16PZN synthesized through the conventional solid state reaction was ~8800 when measured at a frequency of 1 kHz.

Pioneered by Benjamin [10], mechanical alloying (MA) was originally devised for synthesizing alloys and intermetallics. It has recently been modified to synthesize functional ceramics, whereby the starting compositions were subjected to a significant refinement in particle and crystallite sizes, together with a degree of amorphization, prior to the nucleation and growth of the designed ceramic phases [11]. Several lead-based electroceramics have been prepared in the authors' laboratory by mechanically activating the constituent oxides, including PMN [11], PMN–PT [12], PZT [13] and PZN [14,15]. As the mechanical activation of mixed oxides resulted in the formation of nanocrystalline perovskite phases at room temperature, the multiple steps of calcination at high temperatures commonly employed in conventional ceramic processing routes for phase formation of these electroceramic materials were skipped. The activation-derived electroceramics exhibit a refined microstructure, high sintered density, and therefore excellent electrical properties. In more recent studies, attempts were made to

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synthesize PFW [16] and PFW–PZN [17] by further refining the novel technique. On the one hand, PFW cannot however be formed, although PbWO_4 and pyrochlore phases are triggered by mechanical activation. This is in contrast to most other Pb-based relaxor ferroelectric systems such as PMN, PMN–PT and PZT, where the transitional phases were not observed prior to the formation of perovskite phases. On the other hand, nanocrystalline perovskite PZN phase can be steadily formed by mechanically activating the constituent oxides at room temperature, although it cannot be synthesized by the conventional solid state reaction [14]. A number of transitional phases were observed in the ternary PFN–PFW–PZN system when the conventional solid state reaction is employed for phase formation from mixed oxides and they strongly affect the dielectric properties of PFN–PFW–PZN [9]. The objectives of this work are two-fold: (i) to study the feasibility of synthesizing a nanocrystalline perovskite phase in the ternary system which is of interest for a number of applications, by mechanically activating the constituent oxides at room temperature, instead of by calcination at high temperature; and (ii) to characterize the activation-derived PFN–PFW–PZN for phase development, sintering behavior and dielectric properties. A close comparison was made between the material derived from mechanical activation and that derived from the conventional solid state reaction.

2. Experimental procedure

Powder compositions of 0.48PFN–0.36PFW–0.16PZN were prepared by mechanically activating the constituent oxides of PbO , Fe_2O_3 , Nb_2O_5 , WO_3 and ZnO at room temperature. The starting materials used were commercially available PbO (99% in purity; Fluka, Switzerland), Fe_2O_3 (99% in purity; BDH, UK), Nb_2O_5 (99.9% in purity; Fluka, Switzerland), WO_3 (99% in purity; Fluka, Switzerland) and ZnO (99.0% in purity; Merck, Germany). Appropriate amounts of these oxides as required by the stoichiometric 0.48PFN–0.36PFW–0.16PZN were mixed together by conventional ball milling using zirconia balls of 5 mm in diameter in ethanol. A batch of 6 g of the oxide mixture was loaded into a wear resistant cylindrical vial of 40 mm in diameter and 60 mm in length together with one stainless steel ball of 20.0 mm in diameter. Mechanical activation was performed on a shaker mill operated at 900 rpm for various duration's ranging from 5 to 25 h [13,14]. Phase analysis of the resulting powders were carried out using an X-ray diffractometer (XRD, Philips X'Pert, $\text{Cu K}\alpha$). The mechanically activated powders were then characterized for particle size and morphology using a transmission electron microscope (TEM, JOEL-100CX). They were then compacted into pellets of 10 mm in diameter and 2 mm in thickness at a uniaxial pressure of 125 MPa, followed by an isostatic pressing at 350 MPa.

The powder compacts were sintered at 750, 800, 820, 850 and 900°C for 45 min in covered alumina crucibles. Phase analysis was then carried out on the sintered pellets using XRD. The perovskite yield for each pellet was worked out on the basis of the relationship: Perovskite yield (%) = $100 \times I_{\text{per}} / (I_{\text{per}} + I_{\text{pyro}})$, where I_{per} and I_{pyro} are the peak intensities for perovskite (110) and pyrochlore (222) phases, respectively [6]. The density of each sintered ceramic was measured using the Archimedes method in deionised water. Their fracture surfaces were characterized using Scanning Electron Microscope (SEM, Philips XL30). They were then measured for dielectric properties using a LCR meter (Hewlett Package HP 4284A) at various frequencies ranging from 0.1 to 100 kHz over the temperature range of -50 to 150°C .

3. Results and discussion

Fig. 1 shows the XRD patterns of the oxide mixtures equivalent to 0.48PFN–0.36PFW–0.16PZN in composition when mechanically activated for various durations ranging from 5 to 25 h, together with that of the powder mixture without subjecting to any activation. The XRD pattern for the latter shows distinct peaks belonging to the starting oxides of PbO , Fe_2O_3 , Nb_2O_5 , WO_3 and ZnO , indicating

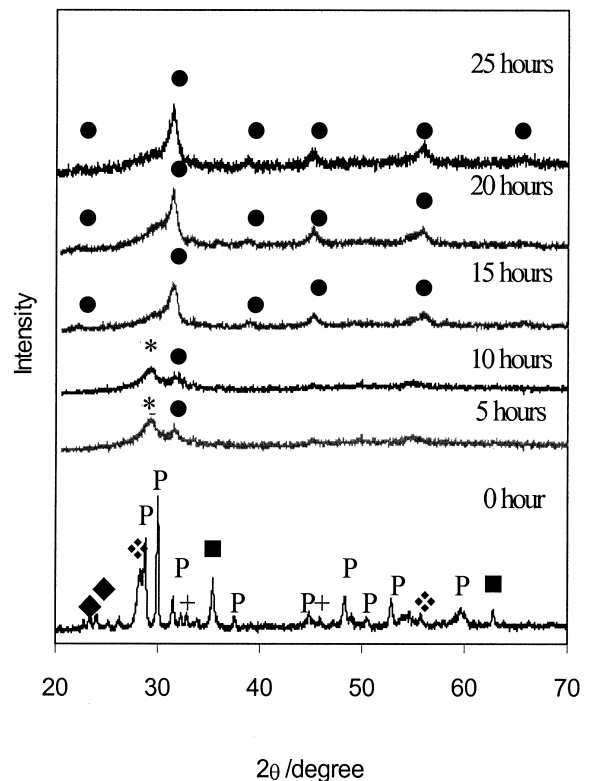


Fig. 1. XRD patterns of the mixed oxides of PbO , Fe_2O_3 , WO_3 , Nb_2O_5 and ZnO equivalent to 0.16PZN–0.48PFN–0.36PFW in comparison when mechanically activated for 0, 5, 10, 15, 20 and 25 h. (P: PbO , ■: Fe_2O_3 , ◆: WO_3 , ⋄: Nb_2O_5 , +: ZnO , *: Pyrochlore).

that little if any reaction, occurred among the mixed oxides during the conventional ball mill mixing. The strongest peak at a 2θ angle of 29.0° corresponds to the principal peak of PbO (111). Upon 5 h of mechanical activation, all the sharp peaks belonging to the starting oxides have disappeared and are replaced by two distinct broadened peaks over the 2θ angle of 28 to 32° centered at 29.3° and 31.1° , respectively. They correspond to the principal peaks of pyrochlore and perovskite phases, respectively. There are several pyrochlore phases that can occur in the conventional solid state reaction among the mixed oxides of PbO, Fe_2O_3 , Nb_2O_5 , WO_3 and ZnO, depending on the calcination temperature [9]. However, the sequence of reactions and the types of transitional phase involved in the mechanical activation of mixed oxides are significantly different from those in the conventional solid state reaction. For example, $\text{Pb}_3\text{Nb}_4\text{O}_{13}$, $\text{Pb}_2\text{Nb}_2\text{O}_7$ and other pyrochlore phases were not observed in mechanical activation of mixed oxides for PMN, PZN, and PMN–PZN–PT, although they steadily occur in the conventional solid state reactions [18,19]. In contrast, the pyrochlore-type $\text{Pb}_2\text{FeWO}_{6.5}$ phase occurred in the mixed oxides of PbO, Fe_2O_3 and WO_3 upon mechanical activation [16]. It appears that the pyrochlore phase in Fig. 1 for the compositions subjected to 5 and 10 h of mechanical activation resembles that formed among PbO, Fe_2O_3 and WO_3 upon mechanical activation. This can be attributed to the poor reactivity of Fe_2O_3 and ZnO as observed in the conventional solid state reaction [20]. There was little change in the XRD trace when the mechanical activation is extended to 10 h. However, the pyrochlore phase was minimized at 15 h of mechanical activation, and an essentially single phase of nanocrystalline perovskite structure was obtained, as illustrated by the XRD peaks at 2θ angles of 31.5° , 45.0° and 56.2° corresponding to the three principal peaks of perovskite phase, respectively. Not much change is observed in the XRD trace with further increase in activation time up to 25 h. These phase analysis results suggest that the initial 5 h of mechanical activation results in a significant refinement in particle and crystallite sizes and a degree of amorphization of the constituent oxides, while the formation of pyrochlore and perovskite phases were triggered at room temperature. This is supported by the increase in specific surface area with increasing mechanical activation time. For example, the powder mixture without subjecting to any mechanical activation exhibited a specific surface area of $1.1 \text{ m}^2 \text{ g}^{-1}$. Mechanical activation for 5, 10 and 15 h resulted in a steady rise in the specific surface area, which levels off at $4.5 \text{ m}^2 \text{ g}^{-1}$ at 15 h of mechanical activation. The transitional pyrochlore phase is evidently unstable against further mechanical activation and it has almost completely disappeared at 15 h of activation.

To illustrate the effects of mechanical activation on the particle characteristics, Fig. 2a–c are three bright field TEM micrographs for the powder mixtures that were not

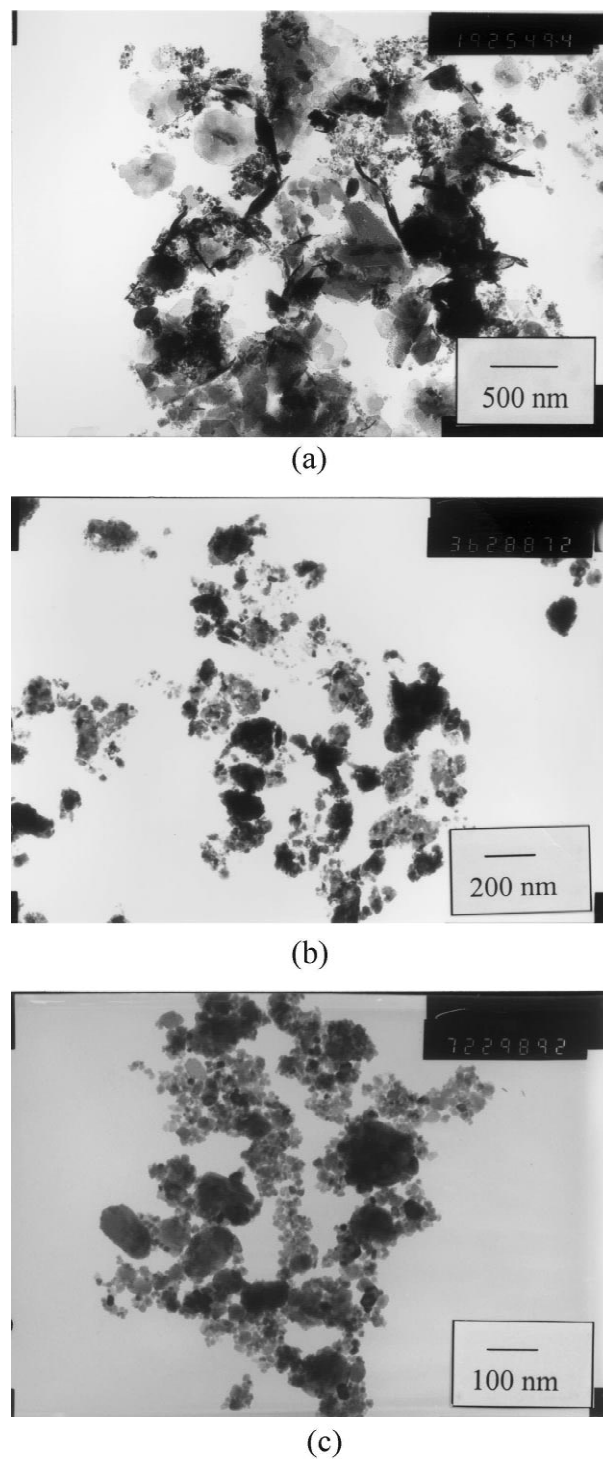


Fig. 2. Bright field TEM micrographs for mixed oxides of PbO, Fe_2O_3 , Nb_2O_5 , WO_3 and ZnO equivalent to 0.48PFN–0.36PFW–0.16PZN: (a) without subjecting to any mechanical activation, (b) subjected to 20 h, and (c) subjected to 25 h of mechanical activation, respectively.

subjected to any mechanical activation and that were mechanically activated for 20 and 25 h, respectively. The starting powder mixture consists of large PbO particles, which are irregular in morphology, together with the irregularly shaped particles of constituent oxides of Fe_2O_3 ,

Nb_2O_5 , WO_3 and ZnO . Their particle sizes are in the range of submicrons. Upon 20 h of mechanical activation, more or less spherical particles of 10 to 20 nm in size are observed, although a degree of particle agglomeration has occurred. Further increasing the mechanical activation time to 25 h, however resulted in an increase in the degree of particle agglomeration, although the discrete particles remain in the nanometer range. This adversely affected the sintered density and dielectric properties of 0.48PFN–0.36PFW–0.16PZN. Therefore, the composition derived from 20 h of mechanical activation was chosen for further study in the phase development and densification with increasing sintering temperature.

Phase developments with increasing sintering temperature in the powder compacts that were not subjected to any mechanical activation and that were mechanically activated for 20 h are shown in Figs. 3 and 4, respectively. As shown in Fig. 1, no mechanochemical reaction occurred when the five constituent oxides were mixed together in the conventional ball mill. Perovskite phase was developed when the powder pellets of mixed oxides were sintered for

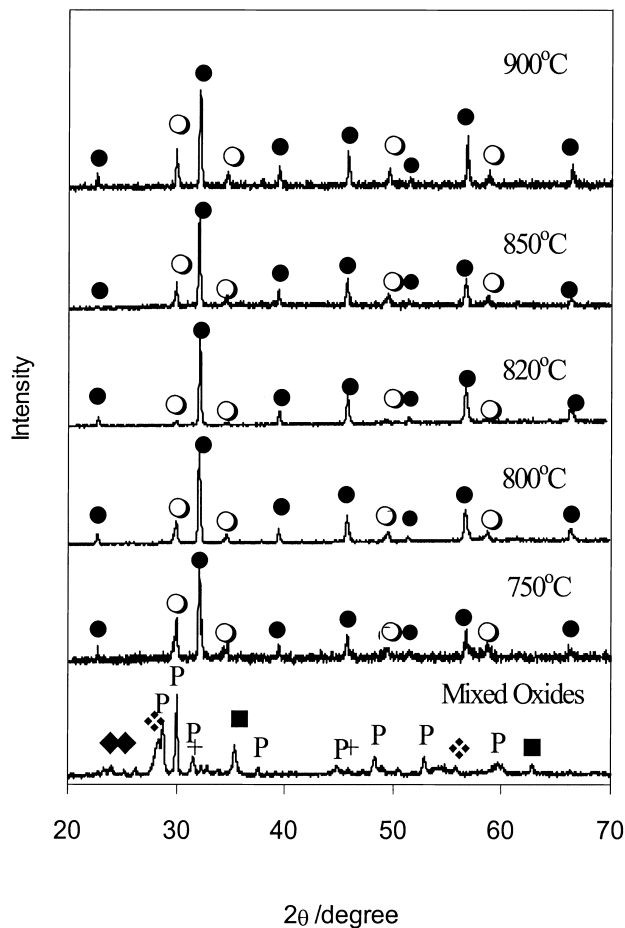


Fig. 3. XRD traces for 0.16PZN–0.48PFN–0.36PFW derived from mixed oxides without subjecting to any mechanical activation and sintered at various temperatures ranging from 750 to 900°C. (P: PbO , \blacksquare : Fe_2O_3 , \blacklozenge : WO_3 , \blacktriangledown : Nb_2O_5 , \blackplus : ZnO , \bullet : Perovskite, \circ : Pyrochlore).

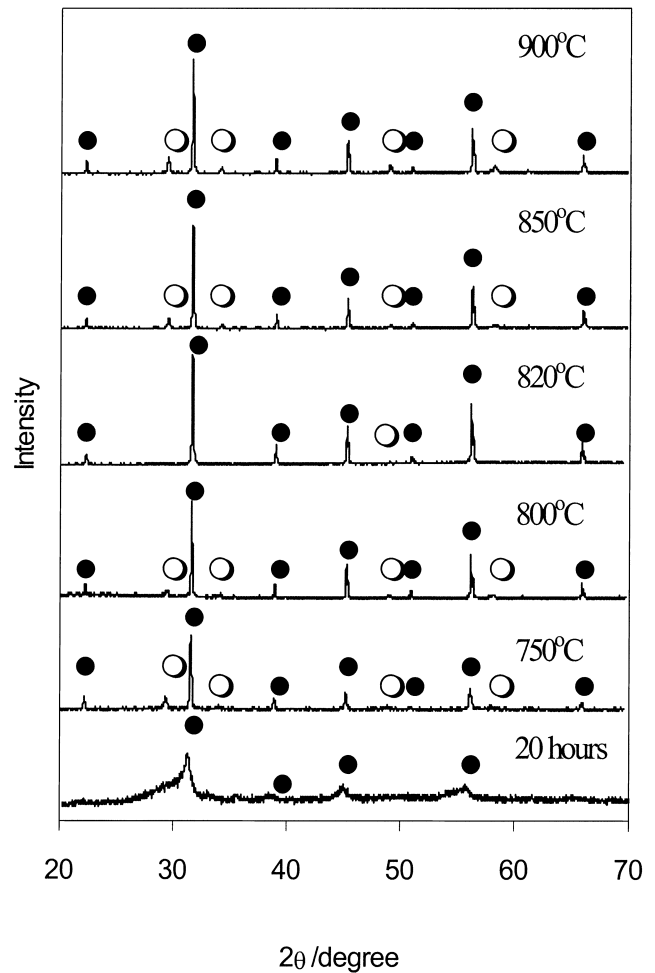


Fig. 4. XRD traces for 0.16PZN–0.36PFW–0.48PFN derived from the mixed oxides subjected to 20 h of mechanical activation and sintered at various temperatures ranging from 750 to 900°C. (\bullet : Perovskite, \circ : Pyrochlore).

45 min at various temperatures ranging from 750 to 900°C. This is observed in the XRD patterns of Fig. 3, where the peaks at 2θ angles of 31.5, 45.0 and 56.2° correspond to the perovskite (110), (200) and (211) planes, respectively. Varying amounts of pyrochlore phase, which was studied by Kassarijan et al. [9] in the mixed oxides of PbO , Fe_2O_3 , Nb_2O_5 , WO_3 and ZnO , occurred at all sintering temperatures as indicated by the diffraction peaks at 2θ angles of 29.3, 34.0, 48.9 and 58.2°. The amount of pyrochlore phase decreases with increasing temperature from 750 to 820°C, where it minimizes. However, it is redeveloped when the sintering temperature is raised from 820 to 900°C. It is therefore difficult to obtain a single perovskite phase from the oxide mixture without pre-sintering mechanical activation in the powder state. In contrast, as shown in Fig. 4, the materials derived from the powder composition subjected to 20 h of mechanical activation and sintered at 750, 800, 850 and 900°C exhibit perovskite as the predominant phase, although there is a minor amount of pyrochlore phase present. Apparently, at each of these sintering

temperatures, the amount of the undesirable pyrochlore phase is lower than that in the powder pellet derived from the powder without subjecting to any activation. Furthermore, a single perovskite phase was achieved in the pellet derived from the powder mixture mechanically activated for 20 h when sintered at 820°C for 45 min. This sintering temperature is apparently lower than those reported for the materials of similar composition processed via the conventional mixed oxide route [2,6]. The mechanical activation apparently led to the formation of a perovskite phase of nanocrystallinity in the multi-oxide system, which is traditionally realized by the solid state reactions at elevated temperatures involving several undesirable transitional phases. Fig. 5 plots the perovskite yield as a function of sintering temperature for 0.48PFN–0.36PFW–0.16PZN derived from the powders mechanically activated for 20 h and that was not activated. There is a sharp rise in the amount of perovskite phase with increasing sintering temperature from 89% at 750°C to 100% at 820°C for the composition subjected to 20 h of mechanical activation. This is followed by a drop to ~93% at 850°C and finally to 86% at 900°C. The perovskite yield also increases with increasing temperature in the unactivated composition, from 73% at 750°C to 80% at 800°C before it peaks at 96% at 820°C. This is then followed by a drop to 91% at 850°C and finally to 78% at 900°C. These phase analysis results show that while a single phase perovskite phase can

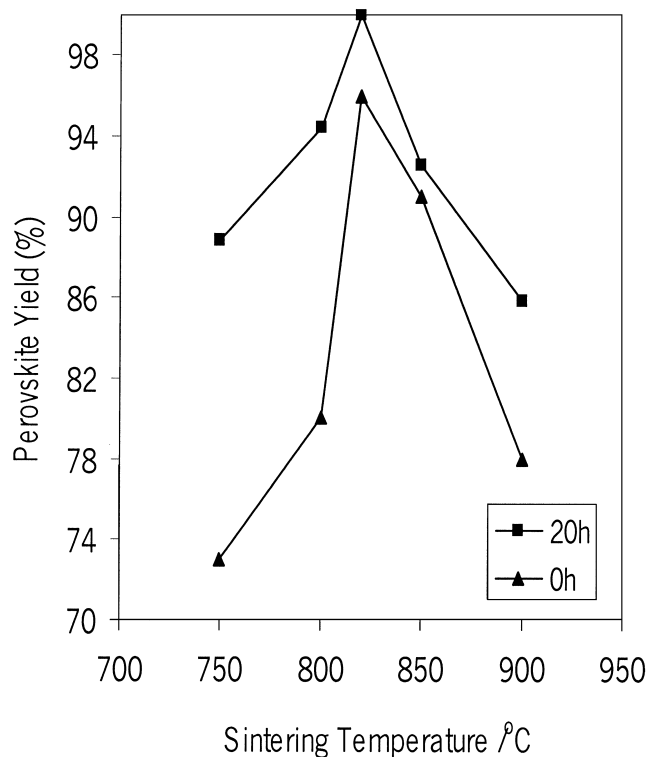


Fig. 5. Dependence of perovskite yield on the sintering temperature of 0.16PZN–0.36PFW–0.48PFN subjected to 20 h of mechanical activation and without subjecting to any activation.

be obtained from the powder mechanically activated for 20 h, it is impossible to achieve a single perovskite phase when the mixed oxides are not mechanically activated.

Fig. 6 is a plot showing the dependence of sintered density of 0.48PFN–0.36PFW–0.16PZN on the mechanical activation time when sintered for 45 min at 800, 820 and 850°C, respectively. Mechanical activation for 5 h results in a sharp rise in sintered density from ~70 to ~87% theoretical when sintered at 800°C. The increase in rate is then slowed down when mechanical activation is further extended to 15 h, where a sintered density of ~90% was obtained. A further increase in mechanical activation time to 20 h led to a slight further increase in the sintered density to ~92% theoretical. A similar trend in the dependence of sintered density on mechanical activation time is also observed at the sintering temperatures of 820 and 850°C, respectively, i.e. there is a sharp rise in the sintered density at the initial 5 h of mechanical activation, followed by a steady increase when mechanical activation is extended to 20 h. However, a much higher sintered density is observed at 820°C for each mechanical activation time. Sintering at 850°C resulted in an apparent fall in the sintered density. As shown in Fig. 4, a single perovskite phase of 0.48PFN–0.36PFW–0.16PZN was developed at 820°C, where a peak density of ~98% theoretical was also observed. The occurrence of the undesirable pyrochlore phase in the materials sintered at 800 and 850°C, respectively, the presence of which has been

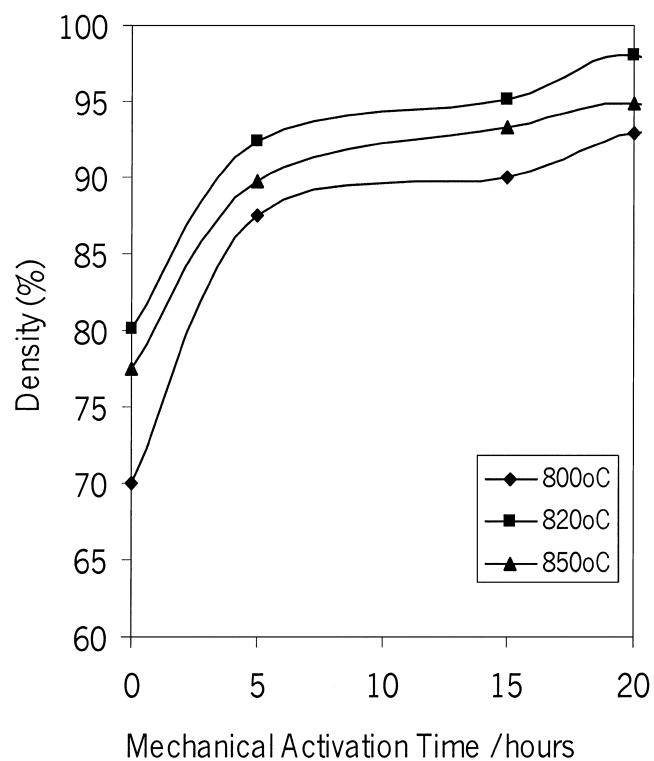


Fig. 6. Dependence of sintered density on mechanical activation time for 0.16PZN–0.36PFW–0.48PFN sintered at 800, 820 and 850°C, respectively.

detected by XRD phase analysis as shown in Figs. 3 and 4, undoubtedly affect the sintered density. The observed improvement in sintered density with increasing mechanical activation time is attributed to the refinement in particle characteristics and the formation of a nanocrystalline perovskite PFN–PFW–PZN phase. Fig. 7 further shows the sintered density as a function of sintering temperature for the materials derived from 20 and 25 h of mechanical activation, respectively. Upon mechanical activation for 20 h, the sintered density of the ceramic peaks at 820°C, apparently due to the development of a single-phase perovskite structure at the sintering temperature. Sintering at temperatures above 820°C results in a fall in the sintered density, coinciding with the perovskite to pyrochlore decomposition. On the other hand, upon mechanical activation for 25 h, the sintered density of the ceramic is much lowered at temperatures below 850°C. This can be accounted for by the occurrence of particle agglomerates in the powder as observed using TEM in Fig. 2c.

An apparent difference exists in fracture surface between the material derived from 20 h of mechanical activation and that derived from the mixed oxides without subjecting to mechanical activation, when both were sintered at 820°C. As shown by the SEM micrographs in Fig. 8a and b, the former exhibits an average grain size of $\sim 1.3 \mu\text{m}$ and the latter an average grain size of $\sim 1.0 \mu\text{m}$. The smaller grain size observed for the latter is associated with the fact that the material was not properly sintered, as

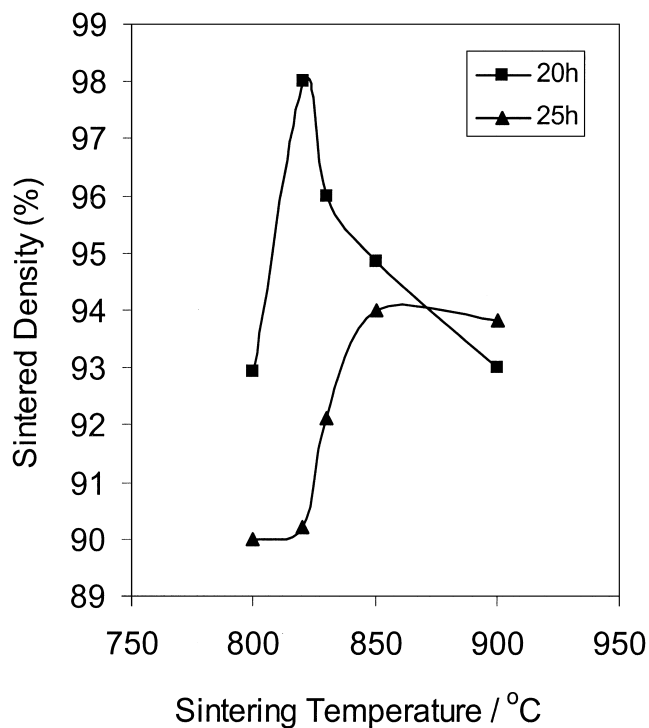
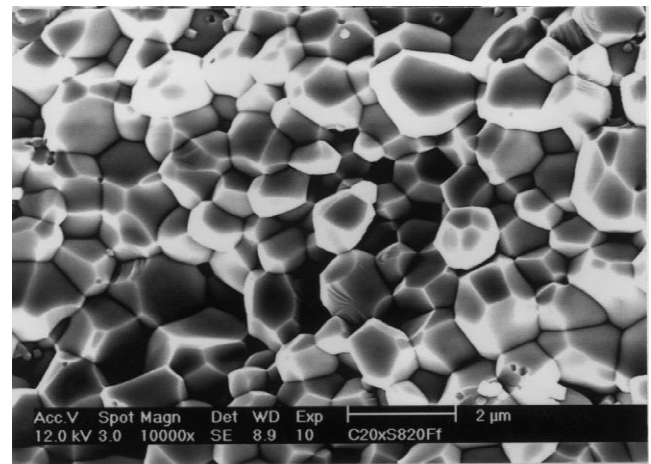
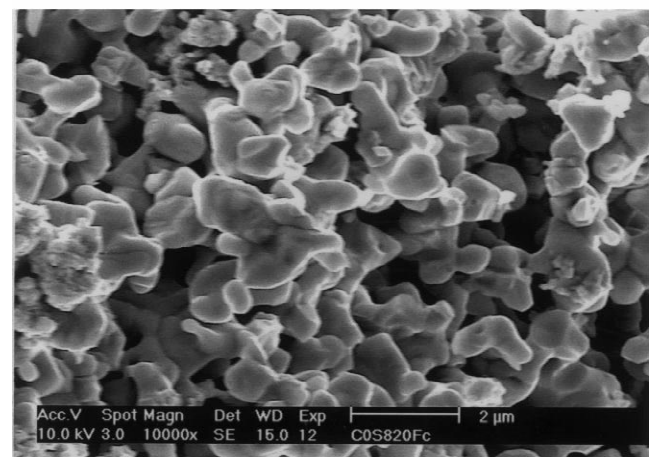


Fig. 7. Effect of sintering temperature on sintered density for 0.16PZN–0.36PFW–0.48PFN derived from the powder subjected to 20 and 25 h of mechanical activation.



(a)



(b)

Fig. 8. Fracture surface of 0.48PFN–0.36PFW–0.16PZN derived from (a) oxide mixture mechanically activated for 20 h and (b) oxide mixture without subjecting to any mechanical activation. Both materials were sintered at 820°C for 45 min.

evidenced by a very porous fracture surface. In comparison, 20 h of mechanical activation led to a dense microstructure of sintered 0.48PFN–0.36PFW–0.16PZN, which agrees with a relative density of 98% theoretical as measured using the Archimedes technique. It exhibits a predominantly intergranular fracture with a more or less equiaxial grain morphology, in contrast to the irregular grain morphology observed for the material derived from the mixed oxides without subjecting to any mechanical activation.

Fig. 9 plots the relative permittivity and dielectric loss as a function of test temperature at various frequencies for 0.48PFN–0.36PFW–0.16PZN derived from 20 h of mechanical activation and sintered at 820°C for 45 min. The relaxor characteristic of the ternary composition is evident from the broad transition and frequency dispersion. It exhibits a maximum dielectric permittivity of ~ 9357 at the Curie temperature of 27°C when measured at 100 Hz. The

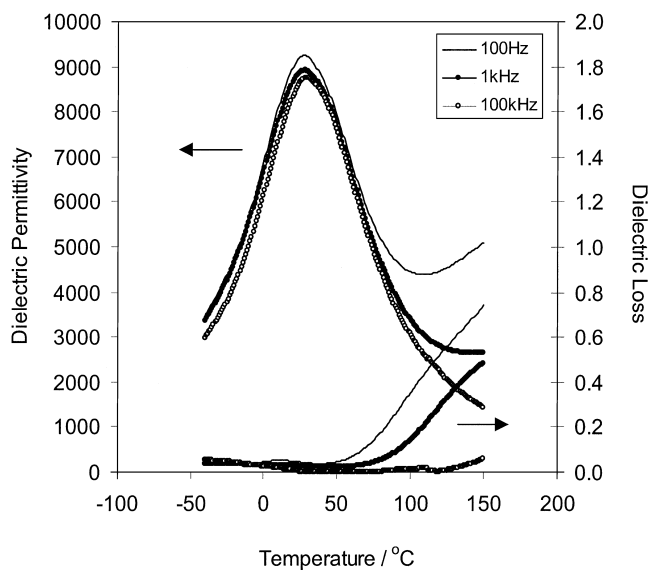


Fig. 9. Dielectric permittivity and loss as a function of temperature for 0.16PZN–0.48PFN–0.36PFW derived from 20 h of mechanical activation and sintered at 820°C.

high dielectric constant can be attributed to a single perovskite phase formed at 820°C, together with a high sintered density. As a comparison, the ceramic derived from the powder without any mechanical activation and sintered at 820°C exhibits a much lower dielectric permittivity (<500) at the Curie temperature of 1°C, apparently due to the occurrence of pyrochlore phase and poor sintered density. The dielectric loss of the material derived from 20 h of mechanical activation remains rather low at temperatures below 50°C. The subsequent rise at temperatures above 50°C in dielectric loss can be accounted for by the minor amount of Fe contamination (equivalent to ~0.2 wt.% Fe₂O₃ as calculated from the weight loss of stainless vial and milling ball) introduced during the 20 h of mechanical activation.

4. Conclusions

A predominant perovskite phase has been synthesized in the multi-component system 0.48PFN–0.36PFW–0.16PZN

by mechanically activating mixed oxides of PbO, Fe₂O₃, Nb₂O₅, WO₃ and ZnO for more than 15 h at room temperature. A dense PFN–PFW–PZN of single perovskite phase is then obtained by sintering the activated powder composition at 820°C, although the perovskite phase derived from 20 h of activation undergoes a partial decomposition upon heat treatment to a pyrochlore phase. It was sintered to ~98% theoretical density at 820°C for 45 min. This is in strong contrast to the porous structure of the ceramic derived from the oxide mixture without subjecting to any activation prior to sintering. The former exhibits a maximum dielectric permittivity of ~9357 at 100 Hz.

References

- [1] M. Yonezawa, *Am. Ceram. Soc. Bull.* 62 (1983) 1375.
- [2] G. Drazic, M. Trontelj, D. Kolar, *J. Mater. Sci.* 25 (1990) 2590.
- [3] M. Yonezawa et al., United States Patent, 4236928, 1980.
- [4] K. Okazaki, *Ceram. Bull.* 67 (1988) 1946.
- [5] M.P. Kassirjian, R.E. Newnham, J.V. Biggers, *Am. Ceram. Soc. Bull.* 64 (1985) 1245.
- [6] R. Naterajan, J.P. Dougherty, *J. Mater. Sci.* 33 (1998) 1991.
- [7] G. Drazic, M. Trontelj, D. Kolar, *Mater. Sci. Eng. B26* (1994) 189.
- [8] G. Drazic, M. Trontelj, D. Kolar, *J. Mater. Sci.* 28 (1993) 4405.
- [9] M.P. Kassirjian, R.E. Newnham, J.V. Biggers, *Am. Ceram. Soc. Bull.* 64 (1985) 1108.
- [10] J.S. Benjamin, *Sci. Am.* 234 (1976) 40.
- [11] J. Wang, D.M. Wan, J.M. Xue, W.B. Ng, *J. Am. Ceram. Soc.* 82 (1999) 1358.
- [12] J. Wang, D.M. Wan, J.M. Xue, W.B. Ng, *Adv. Mater.* 11 (1999) 210.
- [13] J.M. Xue, D.M. Wan, S.E. Lee, J. Wang, *J. Am. Ceram. Soc.* 82 (1999) 1687.
- [14] J. Wang, D.M. Wan, J.M. Xue, W.B. Ng, *J. Am. Ceram. Soc.* 82 (1999) 477.
- [15] J. Wang, D.M. Wan, J.M. Xue, W.B. Ng, Singapore Patent, 9801566-2, 1998.
- [16] S.K. Ang, J. Wang, D.M. Wan, J.M. Xue, L.T. Li, *J. Am. Ceram. Soc.* 83 (2000) 1575.
- [17] S.K. Ang, J. Wang, J.M. Xue, *Solid State Ionics* 127 (2000) 285.
- [18] A. Mergen, W.E. Lee, *J. Eur. Ceram. Soc.* 17 (1997) 1033.
- [19] T.R. Shrout, A. Halliyal, *Am. Ceram. Soc. Bull.* 66 (1987) 704.
- [20] M. Lejeune, J.P. Boilot, *Ceram. Int.* 9 (1983) 119.