Perovskite Phase Stabilization of $Pb(Zn_{1/3}Ta_{2/3})O_3$ Ceramics Induced by $PbTiO_3$ Seeds

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In this work a new methodology to stabilize the perovskite phase in $(1-x)Pb(Zn_{1/3}Ta_{2/3})O_3-xPbTiO_3$ ($(1-x)$PZTa−xPT) ($x = 0.00-0.80$) ceramics is presented. This approach combines the maximization of the crystalo−chemical and thermodynamics requirements and the optimization of the kinetics of the reaction of the perovskite phase formation by using a highly reactive PT nucleus. At the same time, and for comparison, PZTa−PT ceramics are prepared through a conventional mixed oxide procedure (columbite method). The effect of PT seeds is evaluated on the formation of the perovskite phase, and the microstructure and dielectric properties of PZTa−PT ceramics. Analysis of the phase formation process by DTA and XRD shows that PT seeds promote perovskite formation in the $Pb(Zn_{1/3}Ta_{2/3})O_3$ system at a lower temperature and a lower PT content. A pure perovskite phase is obtained at $x = 0.60$ by the PT seeds method and only at $x = 0.75$ by the mixed oxide method. Dense and homogeneous microstructures are observed for seeded ceramics. The dielectric permittivity maximum of 0.40PZTa−0.60PT seeded ceramics is 13 800, compared with 5800 for the ceramics prepared by the conventional columbite method.

I. Introduction

Lead-based relaxor ferroelectrics with perovskite-type structure exhibit excellent dielectric properties, a broad dielectric maximum, and large piezoelectric and electrostrictive coefficients. Together with the possibility of designing the properties by solid solution formation with other ABO_3 members, relaxor ferroelectric materials are very attractive for multilayer capacitors, piezoelectric transducers, and electrostrictive actuator applications to operate under different frequency and temperature conditions.[1,2] The low phase-transition temperature of some members of the lead-based tantalate family $Pb(B_{1-x}Ta_x)O_3$, in which B is Zn^{2+}, Mg^{2+}, and Ni^{2+}, make them important candidates for utilization in devices such as low-temperature capacitors and actuators for space applications.[3]

Compared to the niobate relaxor compounds, $Pb(B_{1-x}Nb_x)O_3$, not too much attention has been paid to the tantalate family, $Pb(B_{1-x}Ta_x)O_3$. Besides the low phase transition temperature, it has been reported that the synthesis of monophasic compounds is difficult in some compositions of these systems.[4] It is well-known that during the phase-formation process of lead-based perovskite materials a pyrochlore-type phase ($A_2B_2O_{7-\delta}$) with low dielectric permittivity precedes the formation of the perovskite phase. Because of its high stability the pyrochlore is difficult to eliminate and, depending on the systems, it remains as a second phase, degrading the final properties of the material. Hence, from the technological point of view, it is crucial to obtain a single perovskite-phase material in these systems.

Two basic requirements define the thermodynamic stability of the perovskite structure: the relation between the size of the ions and the strength of ionic bonds. The size requirement is defined by the tolerance factor, t [$t = r_A + r_O/\sqrt{2}(r_B + r_O)$], in which r_A and r_B are the average ionic radius at A and B site, respectively, and r_O is the ionic radius of the oxygen. The tolerance factor for a stable perovskite structure should be $0.8 \le t \le 1.09$. The strength of ionic bonds between the cations and the oxygen is quantified by the difference between the electronegativities [$(X_{A-O} + X_{B-O})/2$] and the higher the electronegativity difference is the more stable the perovskite structure is.[5] Unfortunately, most lead-based complex relaxors have a low tolerance factor and low electronegativity difference.[6] From this crystalo−chemical point of view, if lead-based perovskite will be made more ionic or if the tolerance factor will be increased, the pyrochlore phase will be minimized or even eliminated. Several examples prove this statement. $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN) cannot be prepare under atmospheric pressure with the perovskite phase,[7] but it can be stabilized by addition of some perovskite-type compounds, such as 6−7 mol % $BaTiO_3$,[6] 25−30 mol %

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$PbTiO_3$,[6] 15 mol % $BaZrO_3$,[6] 15 mol % $Ba(Zn_{1/3}Nb_{2/3})O_3$,[8] and 9−10 mol % $SrTiO_3$.[9] Similarly to PZN, it has been reported that it is impossible to prepare $Pb(Zn_{1/3}Ta_{2/3})O_3$ (PZTa) with a pure perovskite structure.[4] Several attempts were conducted to obtain the perovskite stabilization in PZTa by adding 80 mol % $Pb(Mg_{1/3}Ta_{2/3})O_3$,[10] and 35 mol % $Ba(Zn_{1/3}Ta_{2/3})O_3$.[11] Kim et al.[12] reported the perovskite formation of $Pb(Zn_{1/3}Ta_{2/3})O_3$ with 80% and 60% of $PbTiO_3$ (PT) substitution, depending on the preparation process. It is thought that the tolerance factor and electronegativity difference in PZN and PZTa systems are increased by the solid solution formation with these compounds.

The above considerations on the stability of the perovskite phase took into consideration only crystalo−chemistry and thermodynamics arguments. But the kinetics of the reaction also plays an important role. It is well-known that by increasing the reactivity of the precursor, homogeneity of the mixture, calcination and/or sintering temperature and time, the amount of the formed perovskite phase increases. Highly reactive powders, synthesized by sol−gel,[13] Pechini,[14] ultrasonic spray pyrolysis,[15] or mechanical activation[16] have been used to prepare PMN-based perovskite-phase lead-based relaxor materials. By changing the order of the sequence of the reaction between the precursors, the pyrochlore phase formation can be bypassed, leading directly to the perovskite phase formation. This method developed by Swartz and Shrout[17] for the preparation of pure $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) is called Columbite (or wolframite). The process of pre-reacting B-site cations, either to form a columbite phase $B'B''_2O_6$ (in the $Pb(B'_{1/3}B''_{2/3})O_3$ systems) or to form a wolframite phase $B'B''_2O_4$ (in the $Pb(B'_{1/2}B''_{1/2})O_3$ systems) has been reported to be successful in the preparation of pure perovskite $Pb(Ni_{1/3}Nb_{2/3})O_3$ (PNN), $Pb(Mg_{1/3}Ta_{2/3})O_3$ (PMT), and $Pb(Sc_{1/2}Ta_{1/2})O_3$ (PST),[18] among others. However it is impossible to synthesize $Pb(Zn_{1/3}Nb_{2/3})O_3$(PZN) and $Pb(Zn_{1/3}Ta_{2/3})O_3$(PZTa) by the columbite method.[4]

In this work a new methodology to synthesize PZTa with the perovskite structure is presented. This approach combines the maximization of the crystalo−chemical and thermodynamics requirements and the optimization of the kinetics of the reaction of phase formation by supplying highly reactive lead titanate nucleus for the formation and stabilization of the perovskite phase. It is expected that nanometric PT perovskite seeds will act as a template for the formation of stable PZTa perovskite. At the same time, and for comparison, PZTa−PT ceramics are prepared from columbite synthesized powders. The effect of PT seeds on the formation of the perovskite phase is analyzed. The microstructure and the dielectric properties of PZTa−PT ceramics prepared by both methods are evaluated and compared.

II. Experimental Section

$(1 - x)$PZTa−xPT ($x = 0-0.80$) ceramics were prepared by two distinct methods: type I − seeds method ($PbO-ZnTa_2O_6-PT$), in which lead titanate nanometric crystalline particles (PT seeds) are introduced; and type II − the columbite method ($PbO-ZnTa_2O_6-TiO_2$), in which the B site oxides, ZnO and Ta_2O_5, are pre-reacted before the reaction with the lead oxide. PT seeds were synthesized by sol−gel method according to the procedure described in the literature.[19] PbAc (lead acetate-3-hydrate, Panreac, 99%) and Ti(i-Pr) (titanium tetra-isopropoxide, Merck, ≥97%) were used as starting reagents. Acetic acid and 1,2-propandiol, which were used as solvents, were added to PbAc. The mixture was stirred until PbAc dissolved completely. Ti(i-Pr) was mixed with acetylacetone. Then the two solutions were mixed by stirring, and at the same time ethanol was added as a solvent to make the final solution with the concentration of 0.4 M. The resulting solution was bright yellow and transparent. The solution was dried at 70 °C for several days until it became a transparent gel. Finally, the dried gel was crushed into powder and calcined at 500 °C for 1 h. The formation of the perovskite phase was checked by XRD (Rigaku D/Max-B) analysis. The particle size distribution of powder was determined by using a LS230 Coulter.

In the type I method the starting raw materials were reagent grade PbO (Merck, 99.0%), ZnO (Merck, 99.0%), Ta_2O_5 (ABCR GmbH, 99.8%) and PT seeds. ZnO and Ta_2O_5 oxides were first mixed in Teflon pots with ethanol in 1:1 mol ratio. The mixture was dried and calcined at 1200 °C for 2 h to form $ZnTa_2O_6$. PbO, $ZnTa_2O_6$, and PT seeds were then mixed according to the formula $(1 - x)$PZTa−xPT ($x = 0-0.80$), for 4 h and calcined at 950 °C for 3 h in a covered alumina crucible.

In the type II method the starting raw materials were similar to those used in type I: reagent grade PbO (Merck, 99.0%), ZnO (Merck, 99.0%), Ta_2O_5 (ABCR GmbH, 99.8%), and TiO_2 (Merck, 99.0%). ZnO and Ta_2O_5 oxides were first mixed to form the columbite phase as in type I method. Then $ZnTa_2O_6$ was mixed with PbO, and with TiO_2 according to the formula $(1 - x)$PZTa−xPT ($x = 0-0.80$). All the mixtures were also calcined at 950 °C for 3 h.

The formation of the crystalline phases was checked by XRD analysis. The relative amount of the perovskite phase was determined from the relative intensities of the major XRD peaks of perovskite (110) and pyrochlore (222) phases, according to the relation: $I_{perov(110)}/(I_{perov(110)} + I_{pyro(222)})$.

The phase formation process was analyzed by differential thermal analysis (DTA). The DTA curves were recorded during the heating of each mixture at a heating rate of 10 °C/min. According to the DTA results, calcinations at the DTA peak temperatures were conducted and followed by XRD analysis for the identification of the phase formation process.

$(1 - x)$PZTa−xPT type I and II powders were uniaxially pressed and then isostatically pressed at 200 MPa. The pellets were sintered at 1200−1250 °C for 2 h in air. The microstructures of sintered samples were observed by SEM (Hitachi S4100). For TEM observation (Hitachi H9000-NA), thin specimens were prepared by mechanical polishing followed by ion-beam milling (BAL-TEC Ion Mill (RES 100)). For evaluation of the dielectric properties, gold electrodes were sputtered on both sides of the sample. Dielectric measurements were conducted on an automatic system in which a vertical tubular electric furnace and a HP4284A LCR meter were controlled by a computer. Dielectric properties were measured at 0.1, 1,

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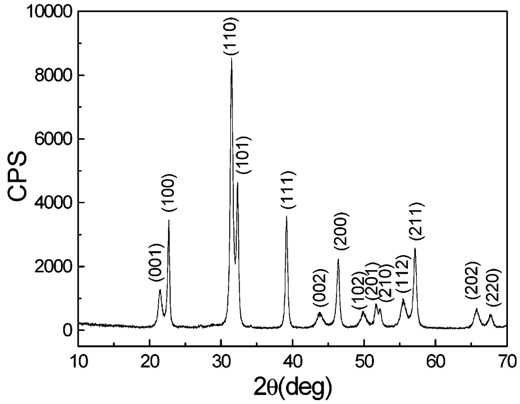

Figure 1. XRD pattern of PT seeds prepared by sol–gel method.

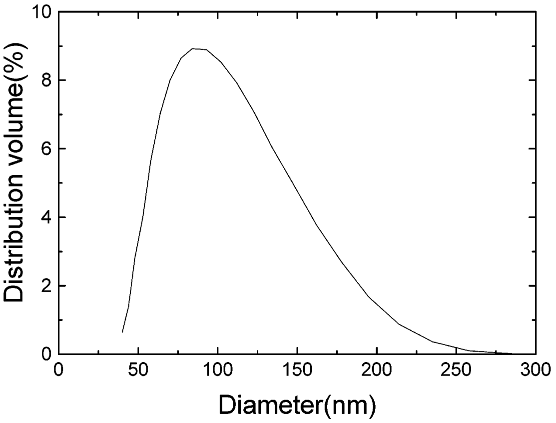

Figure 2. Particle size distribution of PT seeds.

10, and 100 kHz, from room temperature to 400 °C with a heating rate of 2 °C/min.

III. Results

(1) Characterization of PbTiO$_3$ Seeds. The XRD pattern of PT seeds is shown in Figure 1. A pure perovskite phase was obtained after calcination at 500 °C for 1 h. The broadened diffraction peaks indicate a fine grain size of the powder. Figure 2 shows the particle size distribution of PT seeds. PT powders show a fine and a narrow particle size distribution with a mean particle size of 104 nm, which is suitable to use PT powders as seeds.

(2) Phase Formation Process. The chemical reaction and phase evolution processes of both powder mixtures, types I and II, were followed by thermal analysis. The DTA curves obtained for types I and II composition of $x = 0.60$ are shown in Figure 3(a) and (b), respectively. The composition with $x = 0.60$ is the one with the minimum PT content to ensure a pure perovskite phase in PZTa, as will be shown later. Comparing both curves, the differences and similarities are noticed. From room temperature to 500 °C, three endothermic peaks are present in both curves: around 100, 350, and 490 °C for type I mixture (Figure 3(a)) and around 100, 280, and 350 °C for type II mixture (Figure 3(b)). From 550 to 750 °C, one exothermic peak at ~690 °C is observable for type I mixture and two exothermic peaks, around 590 and 680 °C, are observed for type II mixture. Above 750 °C, one exothermic peak is present around 800 and 850 °C for types I and II mixtures, respectively, and one endothermic peak is present around 900 °C for type I mixture.

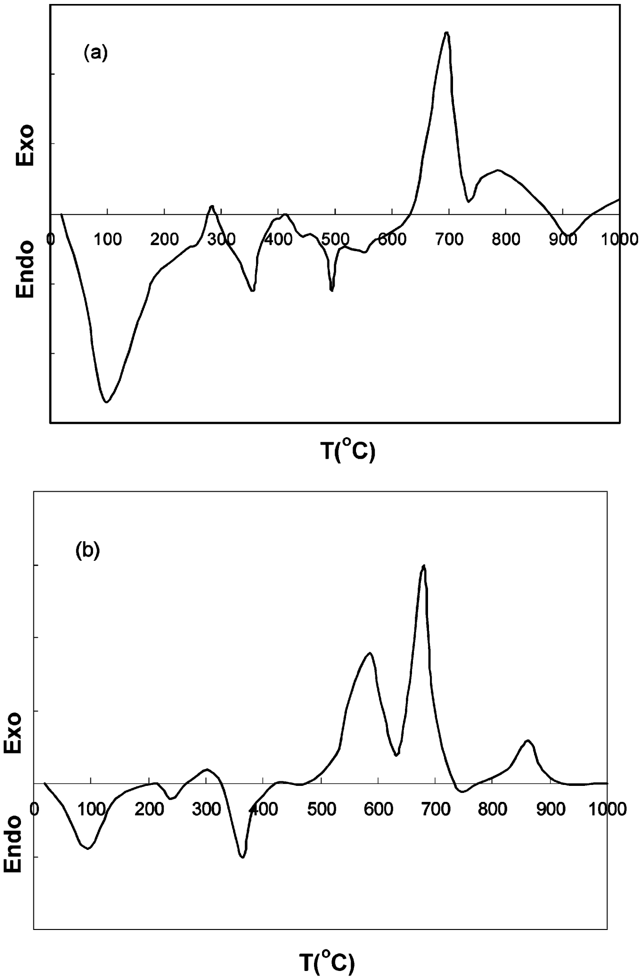

Figure 3. DTA plots at constant heating rate of 10 °C/min in air for PbO–ZnTa$_2$O$_6$–PT(seeds) – type I, and (b) PbO–ZnTa$_2$O$_6$–TiO$_2$ – type II mixtures.

To identify the thermal features observed by DTA, XRD analyses of mixtures calcined at the endo- and exothermic peak temperatures were combined. The endothermic peaks between 100 and 400 °C are assigned to the evaporation of water and decomposition of organic species. The endothermic peak around 490 °C in type I mixture results from the phase transition of PT seeds from the tetragonal ferroelectric to the cubic paraelectric phase. The results of XRD analyses of types I and II mixtures calcined at different temperatures, between 550 and 950 °C, are shown in Figure 4(a) and (b), respectively. At 590 °C the detected phases in type I powders (Figure 4(a)) are massicot PbO, columbite-type ZnTa$_2$O$_6$, perovskite-type PT, and a residual pyrochlore-type phase. By comparison with the RX data files (JCPDS) and the literature[12] the pyrochlore was identified as Pb$_{1.83}$Ta$_{1.71}$Zn$_{0.29}$O$_{6.39}$. For the same calcination temperature the same phases, PbO, ZnTa$_2$O$_6$, perovskite, and also a residual pyrochlore, are visible in the type II mixture. This result indicates that the exothermic peak at 590 °C in type II mixture, and absent in type I, corresponds to the perovskite phase formation of PbTiO$_3$, as confirmed by the XRD analysis (Figure 4(b)). According to the crystalo–chemical and thermodynamic considerations discussed in the Introduction,

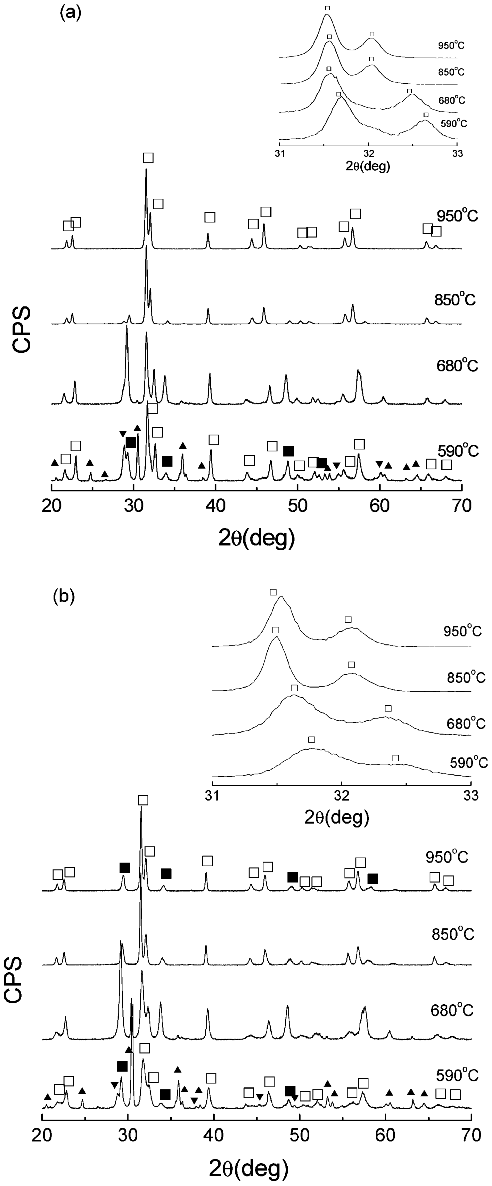

Figure 4. XRD patterns of (a) $PbO-ZnTa_2O_6-PT$(seeds) − type I, and (b) $PbO-ZnTa_2O_6-TiO_2$ − type II, mixtures calcined at different temperatures (☐ perovskite, ■ pyrochlore, ▲ $ZnTa_2O_6$, ▼ PbO).

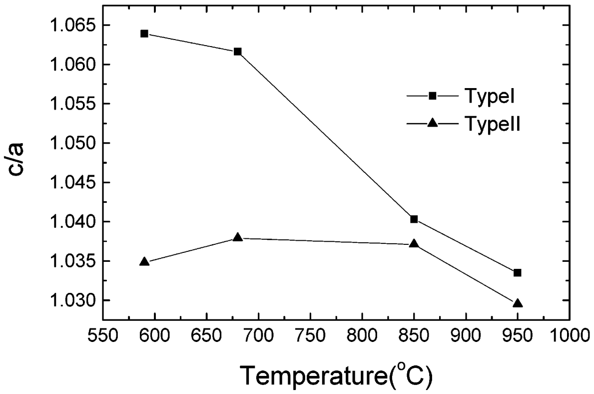

Figure 5. Relationship between calcination temperature and c/a in the perovskite phase ((1 − x)PZTa−xPT of type I and type II mixtures.

the formation of the PT perovskite phase is highly favorable when compared with the PZTa one. This result is similar to the reaction in the $Pb(Zr,Ti)O_3$(PZT) system. In the formation of PZT from $PbO-ZrO_2-TiO_2$ ternary powder mixtures, for a given particle size distribution, PT forms between 450 and 600 °C, followed by PZT formation at temperatures superior to 700 °C.[20] For the type I mixture, as the temperature increases the pyrochlore phase becomes more visible while PbO and $ZnTa_2O_6$ nearly disappear. The exothermic peak at 690 °C is, consequently, attributed to the pyrochlore phase formation. The pyrochlore transforms into the perovskite phase around 800 °C, corresponding to the exothermic peak that is visible in the DTA curve at that temperature (Figure 3(a)). At 850 °C most of the pyrochlore phase had transformed into the perovskite, and pure perovskite is obtained at 950 °C, as shown in Figure 4(a).

For the type II mixture, similar reactions take place. At 690 °C the main detectable phase is pyrochlore, coexisting with PT perovskite and $ZnTa_2O_6$. The pyrochlore was identified as $Pb_{1.83}Ta_{1.71}Zn_{0.29}O_{6.39}$, as in type I mixture. Similarly, the exothermic peak at 690 °C is assigned to the pyrochlore phase formation. Increasing the calcination temperature to 850 °C, the pyrochlore partially transforms into the perovskite phase, accompanied by the disappearance of $ZnTa_2O_6$. The exothermic peak at 850 °C is then attributed to the perovskite phase formation. However, for type II mixture, the pyrochlore phase is still present at 950 °C, as shown in Figure 4(b).

From the XRD patterns depicted in the insets of Figure 4(a) and (b), it is noticeable that the diffraction angles of the perovskite phase shift slightly to the low angle direction with increasing calcination temperature, indicating a compositional change of the perovskite phase. Complimentary to this is the observed variation of the ratio of the c and a lattice parameters (c/a) of the tetragonal perovskite phase with the calcination temperature, shown in Figure 5. As the calcination temperature increases the c/a ratio decreases, markedly for the type I mixture. The decrease of the c/a ratio indicates a decrease of the tetragonality of the perovskite PT lattice and consequently a compositional change of the perovskite. Zn^{2+} and Ta^{5+} ions are being gradually inserted into the perovskite lattice, changing the c/a ratio, as the heat treatment temperature is increasing. For type II mixture, the ratio of c/a slightly increases, then remains unchanged, and decreases with increasing calcination temperature. For the calcination temperature of 590 °C, the ratio of c/a of type II mixture is obviously smaller than that of type I. It indicates that the PT perovskite phase formed at 590 °C has an imperfect (or incipient) crystallographic structure with a low tetragonality. With increasing calcination temperature, the PT perovskite crystal structure is becoming more "organized", resulting in the increase of c/a ratio. But because Zn^{2+} and Ta^{5+} ions are being gradually inserted into the perovskite lattice, the decrease of c/a ratio is observed. Considering that in the case of type I mixture the PZTa−PT perovskite phase nucleates from the tetragonal PT seeds, the decrease of c/a ratio is more obvious than in the case of type II mixture.

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Meanwhile, the diffraction angles of the pyrochlore phase also slightly shift to high angle direction. A similar reaction is occurring with the pyrochlore phase that becomes richer in Ta, changing the composition from $Pb_{1.83}Ta_{1.71}Zn_{0.29}O_{6.39}$ to $Pb_{1.49}Ta_2O_{6.28}$ at higher temperatures. The changing of the lattice constant of $Pb_{1.83}Ta_{1.71}Zn_{0.29}O_{6.39}$ from $a = 10.5982$ Å to $a = 10.5558$ Å of $Pb_{1.49}Ta_2O_{6.28}$ is well consistent with the shifting of 2θ values toward high angles.

According to the above results, the proposed sequence of reactions for the formation of the perovskite phase in the $(1 - x)$PZTa—xPT system is as follows:

(i) for the type I mixture:

$$\mathrm{PbO} + \mathrm{ZnTa_2O_6} + \mathrm{PT(tetragonal)} \xrightarrow{490\ ^\circ\mathrm{C}} \mathrm{PbO} + \mathrm{ZnTa_2O_6} + \mathrm{PT(cubic)}$$

$$\mathrm{PbO} + \mathrm{ZnTa_2O_6} + \mathrm{PT(cubic)} \xrightarrow{680\ ^\circ\mathrm{C}} \mathrm{PbO} + \mathrm{ZnTa_2O_6} + \mathrm{Pb_{1.83}Ta_{1.71}Zn_{0.29}O_{6.39}} + \mathrm{PT}$$

$$\mathrm{PbO} + \mathrm{ZnTa_2O_6} + \mathrm{Pb_{1.83}Ta_{1.71}Zn_{0.29}O_{6.39}} + \mathrm{PT} \xrightarrow{800\ ^\circ\mathrm{C}} \mathrm{Pb_{1.49}Ta_2O_{6.28}} + (1 - x)\mathrm{PZTa}—x\mathrm{PT}$$

$$\mathrm{Pb_{1.49}Ta_2O_{6.28}} + (1 - x)\mathrm{PZTa}—x\mathrm{PT} \xrightarrow{950\ ^\circ\mathrm{C}} (1 - x)\mathrm{PZTa}—x\mathrm{PT}$$

and:

(ii) for the type II mixture:

$$\mathrm{PbO} + \mathrm{ZnTa_2O_6} + \mathrm{TiO_2} \xrightarrow{590\ ^\circ\mathrm{C}} \mathrm{PbO} + \mathrm{ZnTa_2O_6} + \mathrm{PT} + \mathrm{Pb_{1.83}Ta_{1.71}Zn_{0.29}O_{6.39}}$$

$$\mathrm{PbO} + \mathrm{ZnTa_2O_6} + \mathrm{PT} + \mathrm{Pb_{1.83}Ta_{1.71}Zn_{0.29}O_{6.39}} \xrightarrow{680\ ^\circ\mathrm{C}} \mathrm{PbO} + \mathrm{ZnTa_2O_6} + \mathrm{Pb_{1.83}Ta_{1.71}Zn_{0.29}O_{6.39}} + \mathrm{PT}$$

$$\mathrm{PbO} + \mathrm{ZnTa_2O_6} + \mathrm{Pb_{1.83}Ta_{1.71}Zn_{0.29}O_{6.39}} + \mathrm{PT} \xrightarrow{850\ ^\circ\mathrm{C}} \mathrm{Pb_{1.49}Ta_2O_{6.28}} + (1 - x)\mathrm{PZTa} - x\mathrm{PT}$$

$$\mathrm{Pb_{1.49}Ta_2O_{6.28}} + (1 - x)\mathrm{PZTa} - x\mathrm{PT} \xrightarrow{950\ ^\circ\mathrm{C}} \mathrm{Pb_{1.49}Ta_2O_{6.28}} + (1 - x)\mathrm{PZTa} - x\mathrm{PT}$$

The formation of PZTa—PT perovskite phase occurs around 800 and 850 °C for type I and type II mixtures, respectively (Figure 3), indicating that the perovskite phase transformation temperature induced by PT seeds is lower.

Having identified the phase formation process for the PZTa—PT system prepared by both methodologies, it is necessary to analyze the effect of PT content on this process. Figure 6(a) shows the XRD pattern of $(1 - x)$-PZTa—xPT ($x = 0$—0.80) type I powders calcined at 950 °C. For the $x = 0$ composition the main detectable phase is the pyrochlore $Pb_{1.83}Ta_{1.71}Zn_{0.29}O_{6.39}$. Trace amounts of $ZnTa_2O_6$ and PbO are also visible. The perovskite phase is almost not found. As x increases the strongest peaks of this pyrochlore phase are shifted slightly toward the high angle direction, corresponding to another pyrochlore phase, identified as $Pb_{1.49}Ta_2O_{6.28}$. The two kinds of pyrochlores coexist for the compositions with x varying between 0.20 and 0.50. As reported for other lead-based relaxors systems, the phase formation process is complex with the formation of several intermediate phases, namely pyrochlores with varying stoichiometries. As the PT content increases the perovskite phase increases, being clearly visible for $x = 0.30$. For $x \geq 0.60$, a pure perovskite phase with a tetragonal symmetry was obtained, deduced from the clear split of peak around $2\theta = 45°$. The XRD results for type II powders calcined at 950 °C are shown in Figure 6(b) for comparison. The perovskite phase evolution is similar to that observed for type I compositions (Figure 6(a)). However, the pure perovskite is obtained only for $x \geq 0.75$. Figure 7 shows the variation of the amount of perovskite phase formed at 950 °C with the PT content for both methods. It is clear that PT seeds are beneficial for the perovskite stabilization in the PZTa system, allowing a pure perovskite phase to form at lower PT content.

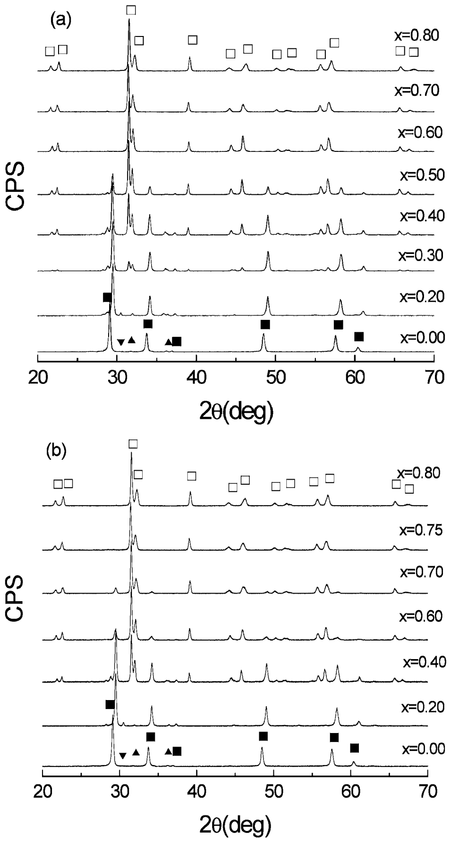

Figure 6. XRD pattern of $(1 - x)$PZTa—xPT powders prepared by (a) type I method and (b) type II method, and calcined at 950 °C (□ perovskite, ■ pyrochlore, ▲ $ZnTaO_6$, ×e2 ▼ PbO).

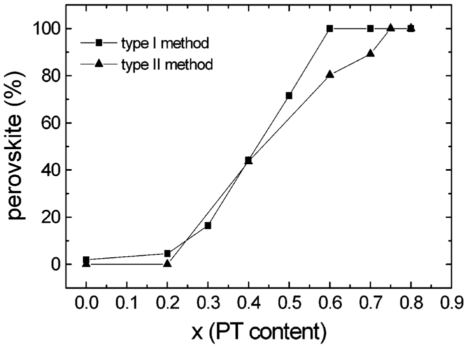

Figure 7. Amount of the perovskite phase in $(1 - x)$PZTa—xPT powders calcined at 950 °C as a function of PT content.

(3) Microstructure and Dielectric Properties. The microstructures of $x = 0.60$ ceramics fabricated with

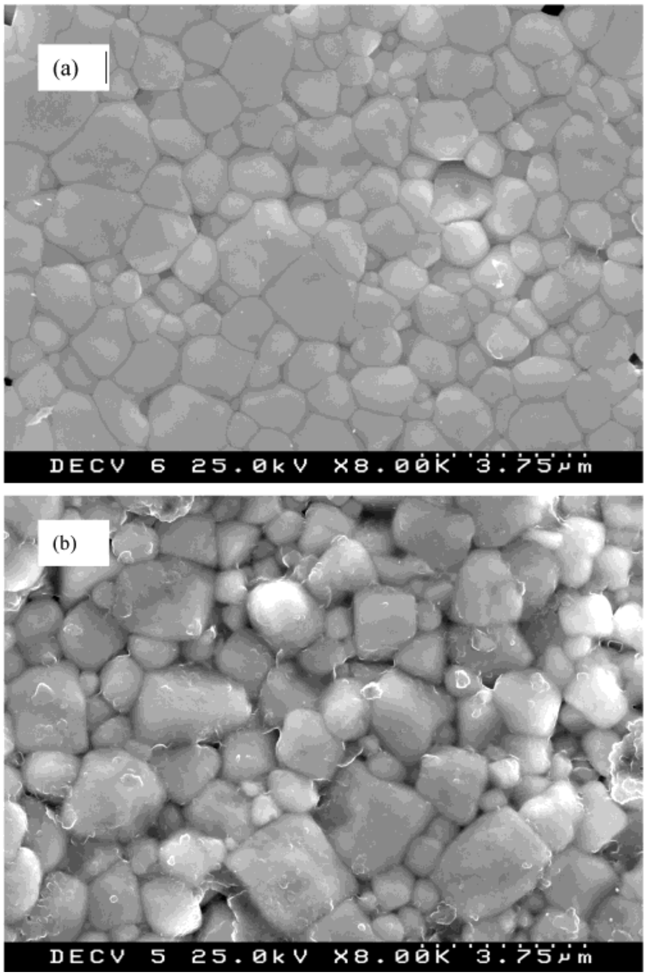

Figure 8. SEM microstructure of (1 − *x*)PZTa−*x*PT (*x* = 0.60) ceramics: (a) type I, and (b) type II.

powders prepared by types I and II methods and sintered at 1250 °C were analyzed by SEM and are shown in Figure 8(a) and (b), respectively. The microstructure of type I sample (Figure 8(a)) is dense and homogeneous, and the grain size varies between 1 and 2 μm. On the other hand, the microstructure of type II sample (Figure 8(b)) is considerably different. The visible intergranular porosity, irregular polyhedral shape of the grains, and inhomogeneous grain size distribution (which varies between 0.3 and 2.5 μm,) clearly evidence the lower degree of densification of these samples.

Figure 9 shows a TEM microstructure of type I (1 − *x*)PZTa−*x*PT ceramics, with *x* = 0.60. It presents clear and clean grain boundaries and a 90° ferroelectric domain structure in the grains, which is attributed to the high tetragonal PT content of the ceramic.

Figure 10 shows the dielectric constant (a) and loss (b) at various frequencies as a function of temperature for *x* = 0.60 ceramics fabricated with the powders prepared by the two different methods. The maximum dielectric constants are 13 800 and 5800 (*f* = 1 kHz) for types I and II, respectively. The dielectric losses for type I samples are lower than that for type II derived samples. It is found that ceramics fabricated by type I method have much higher dielectric constant due to the pure perovskite phase and dense homogeneous microstructure.

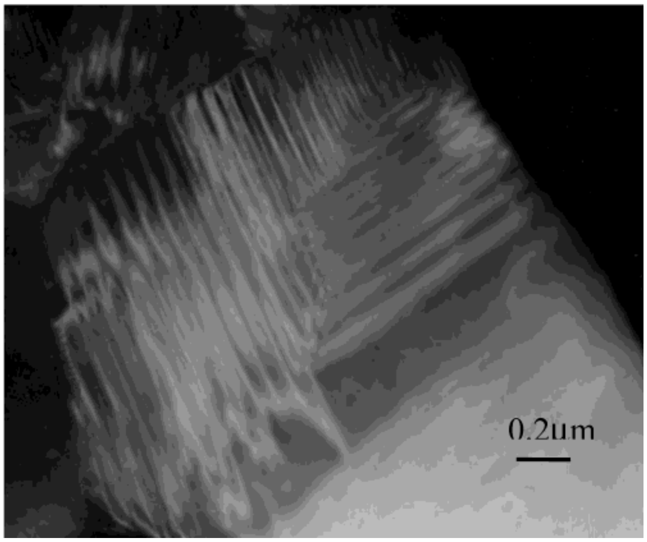

Figure 9. TEM microstructure of (1 − *x*)PZTa−*x*PT (*x* = 0.60) ceramics prepared by type I method.

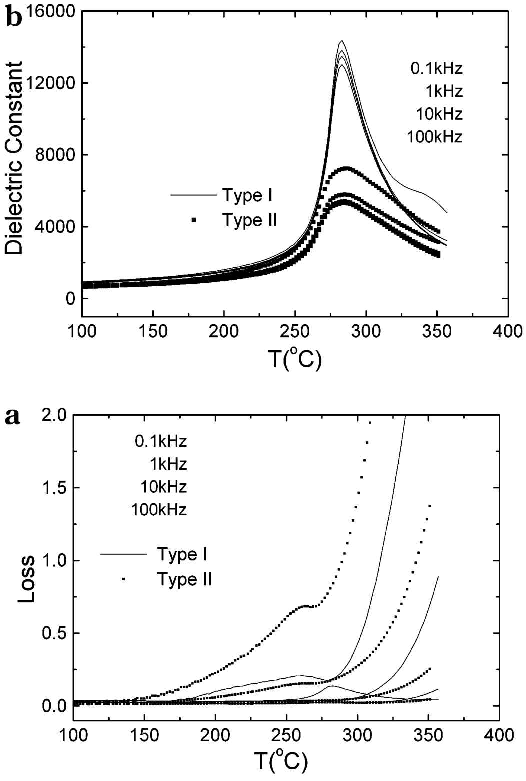

Figure 10. Dielectric constant (a) and loss (b) at various frequencies as a function of temperature for *x* = 0.60 ceramics prepared by type I and II methods.

IV. Discussion

As considered in the Introduction, crystallization of the perovskite phase depends mainly on thermodynamic considerations, but also on the kinetics of the reaction of phase formation. On this basis, a new methodology to synthesize PZTa with the perovskite structure was tried in this work. The maximization of the crystalo−chemical and thermodynamics requirements for the stabilization of PZTa was accomplished by making a solid solution with lead titanate. PT is normal ferroelectric with a stable perovskite structure. The high tolerance factor and high electronegativity difference of

PT increase the thermodynamic stability of the PZTa phase. At the same time, optimization of the kinetics of the reaction of phase formation was achieved by supplying PT as a highly reactive perovskite nucleus prepared by sol−gel (PT seeds) for the formation and stabilization of the perovskite phase.

The seeds method has also been used in preparation of perovskite ferroelectric powders[14,22,23] and films.[19,24,25] The objective of the addition of seeds is to induce formation of the perovskite phase by decreasing the energetic barrier for the phase formation and, consequently, to decrease the formation temperature of the required phase. Cavalheiro et al.[14] studied BT and PT seeding of PMN powders made by the Pechini method. They observed that BT and PT seeds stabilize the PMN perovskite phase under prolonged calcination times. Narendar et al.,[22] studied seeding of perovskite lead magnesium niobate crystallization from Pb−Mg−Nb−EDTA gels. The addition of $BaTiO_3$ seed particles (50 nm diameter) to a Pb−Mg−Nb−EDTA solution reduces the formation temperature of perovskite from 700 to 600 °C during combustion synthesis. Chen et al.[23] studied seeding effects in the sol−gel preparation of lead zirconate titanate (PZT) powders. The formation temperature of pure perovskite phase was lowered by 50 °C with 5 wt % seeds, and a more dense powder microstructure is observed in the presence of seeds. The seeds addition has also been studied in the preparation of thin films. Wu et al.[19] studied seeding effects on crystallization of PZT thin film from sol−gel method. The addition of PZT seeds to the precursor sols was seen to be effective for the crystallization enhancement of the pure perovskite phase at lower temperatures and to improve the dielectric properties of the films.[19]

The results described in the previous section show that PT seeds fabricated by sol−gel method with nanometric particle size have high reactivity. The existence of highly reactive PT seeds supplies an extra nucleus site for the perovskite phase formation. The energy barrier for perovskite phase formation decreases and the stability of perovskite phase in the system increases due to existence of PT seeds. Although the sequence of reaction of phase formation for the type II (columbite) method is similar to that of type I (PT seeds), as indicated from the DTA and XRD analysis study, (Figures 3 and 4), it is noticed that the transformation temperature from pyrochlore to perovskite phase is lower in PT seeds than in the columbite method. This indicates that PT seeds promote the formation of perovskite phase in the PZTa−PT system. Thus, to stabilize the perovskite phase in type II ceramics it is necessary to add a higher $PbTiO_3$ content to the system. PT seeds induce the perovskite-phase formation in the PZTa system, at a lower PT content, when compared with the columbite method. However, even when the PT seeds method is used, the pure perovskite phase in $(1 - x)$PZTa−xPT can only be obtained for $x = 0.60$. As known, the pure perovskite phase in $(1 - x)$PZN−xPT can be obtained when $x = 0.25$.[6] Therefore, the threshold of Ti concentration in PZTa is much higher than that in PZN. So it is more difficult to get pure perovskite phase in tantalate systems than it is in niobates. Although Nb and Ta belong to the same group of the periodic table of elements, Ta^{5+} ($[Xe]4f^{14}\cdot 5d^3\cdot 6s^2$) exhibits one more outer electron than Nb^{5+} ($[Kr]4d^4\cdot 5s^1$). Consequently, Ta^{5+} has stronger covalent properties. As discussed in the Introduction the increase of covalent bond strength will decrease the thermodynamic stability of the perovskite phase. This is the main reason it is more difficult to get perovskite phase in the PZTa systems. Studies on the stabilization of the perovskite phase of PZN and PZTa by BT, PMN, and PMT addition[12] also showed an easier stabilization of the perovskite structure in PZN, due to the higher ionic strength of Nb−O bonds.

The influence of PT seeds is also clearly visible in the microstructure development of the ceramics. A higher degree of densification and a higher homogeneous microstructure was obtained for type I ceramics. The nanometric PT seeds particles, besides acting as templates for the perovskite phase nucleation, act also as nucleus for a homogeneous grain growth in the ceramic. The high surface energy associated with the nanometric PT seeds increase the densification rate, allowing such a microstructure. As a consequence of this improved microstructure the dielectric properties of the PZTa−PT seeded samples are considerable superior to the dielectric properties of the equivalent composition prepared by the columbite method. This constitutes an important result from the technological point of view.

IV. Conclusions

A new approach to stabilize the perovskite phase in the $(1 - x)$ $Pb(Zn_{1/3}Ta_{2/3})O_3$−$xPbTiO_3$ ($x = 0.00-0.80$) system was developed. PT nanometric powders prepared by sol−gel were used to form the solid solution with PZTa. For comparison, identical compositions were prepared by conventional oxides mixture. It was observed that by using PT seeds the pure perovskite phase in $(1 - x)$PZTa−xPT can be obtained at $x = 0.60$, as opposed to $x = 0.75$ for the oxides mixture. Although the process of phase formation is similar in both methodologies, the transformation temperature from pyrochlore to perovskite phase is lower for the seeded compositions. Marked improvements in the microstructure were observed for the seeded ceramics. The dielectric permittivity of 0.40 PZTa−0.60 PT ceramics prepared by PT seeds method is 13 800 at 1 kHz compared with 5800 at 1 kHz for the oxide mixture sample. These results demonstrate that the reaction with nanometric PT seeds is effective to promote stabilization of the perovskite phase in the PZTa system at low temperatures and at a low PT concentration and to improve the microstructure, which allows maximization of the dielectric properties of these ceramics.

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