Relaxation and Dielectrics Properties of Fe-modified PLT Ceramics

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Sol-gel processed PbLay$(Fe_{0.01}Ti_{0.99})_{1-y/4}O_3$ for y = 0, 3, 7, 12, 18 (percentage) ceramic powders have been characterized by X-ray diffraction (XRD) and Raman spectroscopy. Dielectric measurements revealed the existence of interesting features due to the incorporation of Fe in PLT matrix. These results are compared to those of the literature and interpreted.

1. Introduction

Lead titanate $PbTiO_3$ (PT) is a ferroelectric material with interesting physical properties. This makes it suitable for various applications such as capacitors, DRAM and FRAM, electro-optic devices, and so on [1]. PT is known to possess a high Curie temperature (Tc ≈ 490°C), a large tetragonality (c/a = 1.064) and a weak electric permittivity. Addition of lanthanum (La) gives rise to a structural transition from the quadratic to the cubic phase [2,3]. Study of substitution effects of Pb by La (PLT) [4-6] has attracted much attention of researchers due to the specific dielectric and structural properties of PLT. The latter are characterized by a lowering of the temperature of the peak of the ferroelectric to paraelectric transition (FE-PE) and of the grain size, the reduction of the tetragonality, and the increase of the dielectric permittivity [7-10]. PLT shows relaxation behaviour for a content of La around 21%. Substitution of Ti^{4+} ($r_{Ti}{}^{4+} \approx 0.68$Å) by a weak percentage of Fe^{3+} ($r_{Fe}{}^{3+} \approx 0.67$Å) (PLFT) has a great effect on both dielectric and structural properties. Only a few studies relative to PLFT compounds have been reported in the literature. Insertion of Fe in the A site in (Pb, La)(Zr, Ti)O_3 (PLFZT) [11,12] increases the dielectric permittivity, the transition temperature and ameliorates piezoelectric and electromechanical properties. When Fe is substituted in the B site, PLFZT shows relaxation features [13]. Moreover, incorporation of Fe in the B site ($PF_{1/2}T_{1/2}$) [14] decreases the tetragonality, the dielectric permittivity, the Curie temperature, and the grain size [15]. In this work, we have prepared, using the sol gel process, PbLay$(Fe_{0.01}Ti_{0.99})_{1-y/4}O_3$ samples for y = 0, 3, 7, 12, 18 (percentage) PLyF1T. The sol gel process, in addition to its moderate cost, permits a good control of stoichiometrical, physical and chemical homogeneities, as well as favours crystallization at relatively low temperatures [16].

The obtained nanopowders have been characterized with X-Ray diffraction (XRD), and Raman spectroscopy. Besides, dielectric studies revealed particularities of the relaxation phenomenon above a critical concentration in La.

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2. Experience

Crystalline nanopowders of PLyF1T for y = 0, 3, 7, 12, 18, have been prepared using the sol gel process [17,18]. Pb, La and Fe acetates were dissolved in distilled water and few drops of acetic acid (1cc) were added to stabilize the solution and to help dissolving acetates. Ti sol was then added to this solution and a transparent gel of PLyF1T was obtained. The latter was dried in an oven (80°C), grounded and heated at 700°C for 2 hours. For dielectric measurements, the powders were pressed into discs (diam. ≈ 12 mm, thickness ≈ 1.2 mm), without any need of a binder, and heat treated at 1100°C for 4 hours [17-20]. The permittivity was measured with an HP 4284A impedance meter in the frequency range from 100 Hz to 1 MHz.

3. Results and discussion

Fig. 1 shows XRD patterns of PLyF1T for y = 0, 3, 7, 18, calcined at 700°C during 2 hours. The gradual transformation under the addition of La from a tetragonal phase to a pseudo cubic one is clear and no secondary phases were observed except for the sample with y = 3, where the presence of PbO phase is detected [21,22]. The latter is due to the excess of lead acetate (10%) added during the preparation of the samples to compensate its volatilization during heat treatments. This structural change is confirmed by Raman spectra of Fig. 2. Indeed, one can observe in these spectra an enlargement of some peaks, a disappearance of some others and a slight shift of some peaks, in accordance with previous results [23]

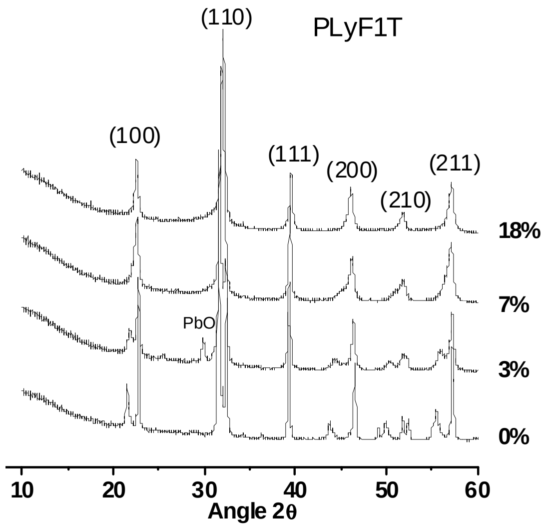

Fig.1: XRD spectra of PLyF1T (y = 0, 3, 7, 18) heat treated at 700°C (2h).

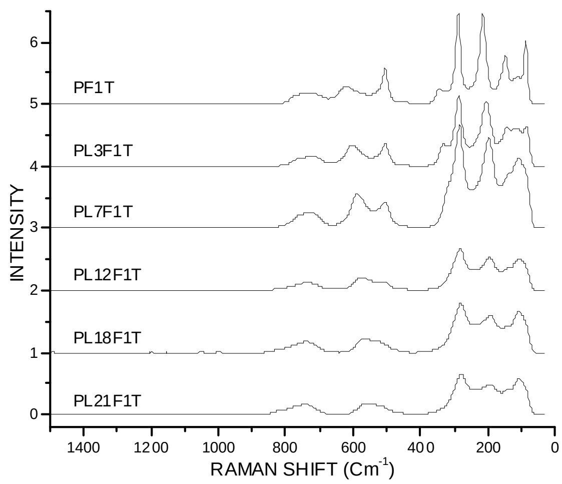

Fig.2: Raman spectra of PLyF1T (y = 1, 3, 7, 12, 18, 21) heat treated at 700°C (2h).

With the help of Scherer formula [24], $D=k\lambda/(\beta_{1/2}\cos\theta)$ for k=1, λ=1.5406Å and where $\beta_{1/2}$ is the half width of the peak (111), we determined the average grain size of the particles (crystallites). Table 1 gathers the corresponding values for the different compositions studied and reveals the presence of relatively small grain sizes on the nanometric scale. The effect of La is shown in Fig. 3, where we observe a reduction of the grain size of the powders. Dielectric measurements were performed on PLyF1T ceramics which were heat treated at 1100 °C (4h). Figs. 4 and 5 reveal that a transition from the ferroelectric to paraelectric phase (FE-PE) occurs at a temperature, Tm, corresponding to the maximum of permittivity, $\varepsilon_r(T)$. A clear diffuse character of this transition together with a relaxation behaviour take place for $y \geq 7$; these two aspects increase with increasing frequency (Fig. 4). Previous studies reported [25, 26] that PLT exhibits relaxation phenomena for a concentration of La equal to 21% and hence from our study one may conclude that addition of Fe lowers this concentration. One can also observe in Fig. 4 that Tm and the permittivity decrease for increasing frequency. Anomalies showing diffuse and relaxation characters are present in the paraelectric phase for the sample with y = 18 in La (Fig. 4). Few studies have reported the presence of such anomalies [27], which may be imputed to oxygen vacancies [28] or to magnetic transitions in compounds with one or more magnetic elements [29]. Concerning the diffuse character of transitions, this phenomenon has been linked to sub micronic chemical in-homogeneities in the samples [30,31]. Then, it may be said that for our samples the addition of La may give rise to the formation of nanodomains of different chemical nature, which break the long range ferroelectric order. Each monodomain brings its own contribution and then Curie temperature; the Gaussian distribution of these local Curie temperatures reveals a diffuse maximum of ε_r.

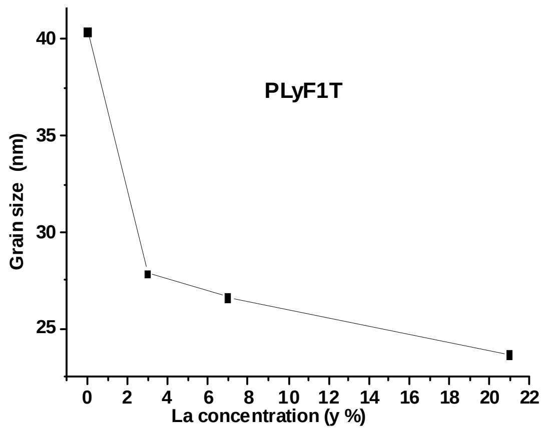

Fig.3: Evolution of the average grain size as a function of La concentration.

Table 1: Average grain size as a function of La concentration.

y	Average grain size (nm)
0	40,41
3	27,91
7	26,65
21	23,69

Our results also show that the maximum of the permittivity, $\varepsilon_{r\ max}$, decreases first for $y \leq 7$ before reaching a maximum for y = 18 in La and then decreases (Fig. 6). The transition temperature Tm decreases linearly as a function of La doping (Fig. 7) and the corresponding slopes decrease with increasing frequencies. As an illustration, this decrease of Tm for the frequency equals 1 kHz may be approached by the equation $T_m = 452.22 - 14.86y$ in accordance with results of reference [32], which reported that the transition temperature is lowered by about 14°C for each mol (%) of La. This result may be due to the reduction of the grain size [33].

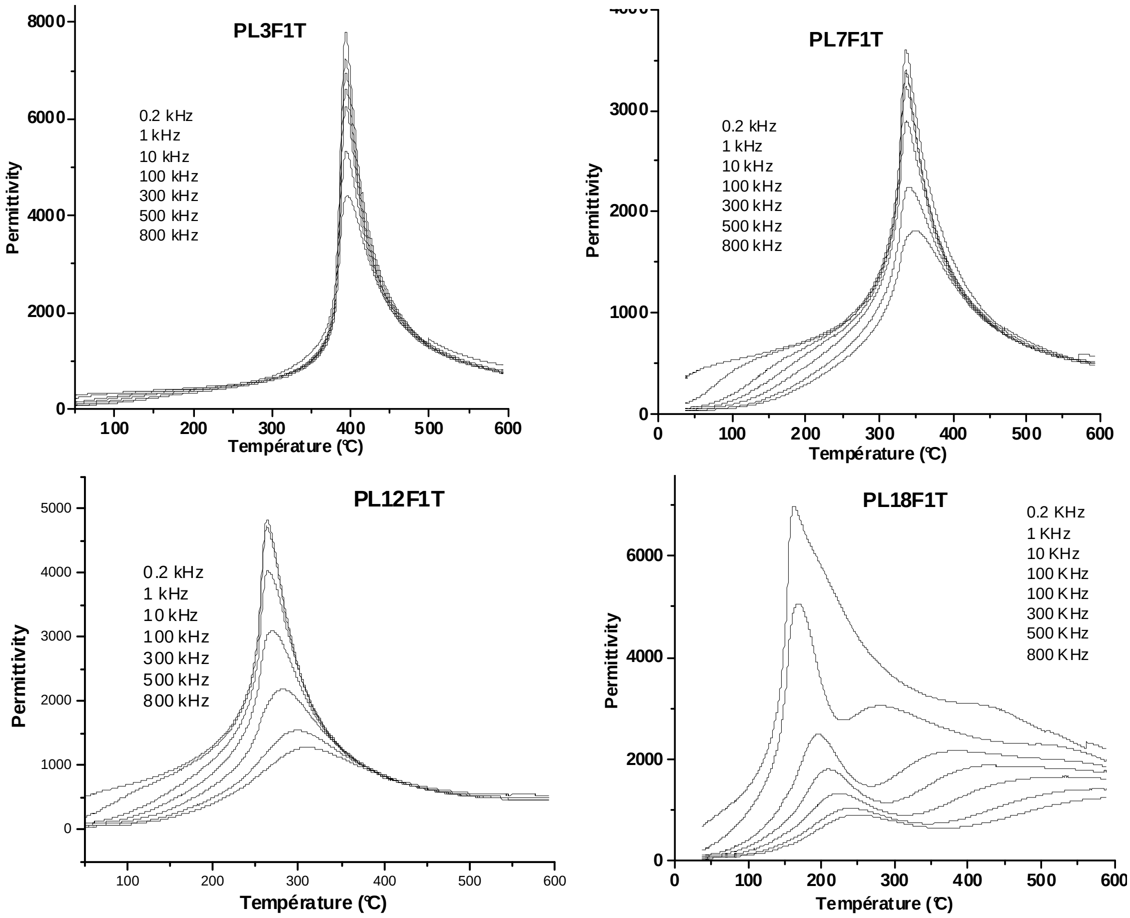

Fig.4: Thermal variations of the permittivity of PLyF1T ceramics for different frequencies.

4. Conclusion

PLyF1T (y=0, 3, 7, 12, 18) powders were prepared using the sol gel process. Characterization with X-rays showed a crystallization of the samples in the perovskite structure, which transforms from tetragonal structure to pseudo cubic one as the content in La is increased; this result was confirmed by Raman spectroscopy. Incorporation of La led to the lowering of the transition temperature, the grain size, and to an increase of the permittivity. Moreover, a small amount of Fe generates relaxation behaviour in PLT ceramics from 7% in La (PL7F1T). Anomalies in the paraelectric phase were detected, the origin of which may come from oxygen vacancies or magnetic transitions; attempts to clarify this point are in progress.

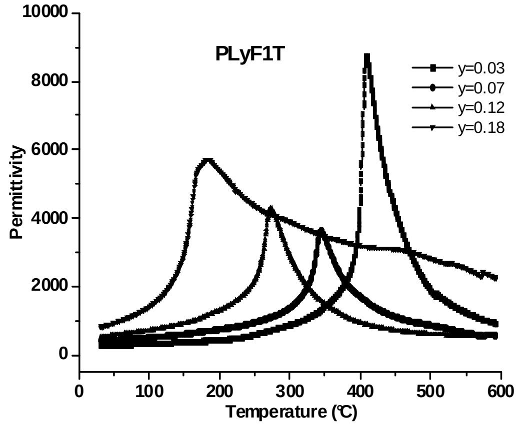

Fig.5: Permittivity of PLyF1T samples with y=0; 3; 7; 12 and 18) for the frequency 0.2 kHz.

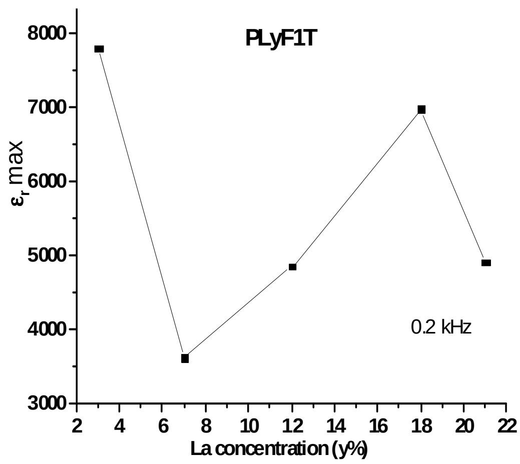

Fig.6: Evolution of $\varepsilon_{r\,max}$ as a function of La concentration.

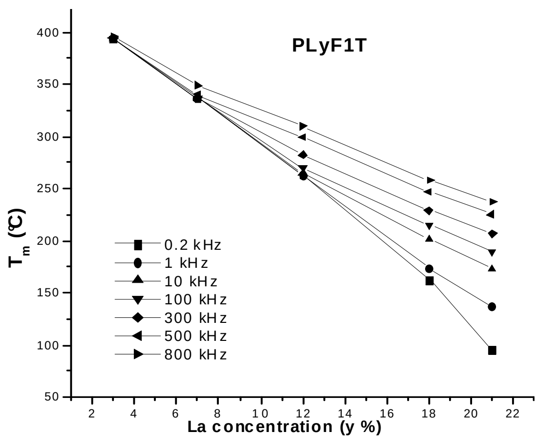

Fig.7: Evolution of T_m as a function of La concentration for different frequencies.

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Received: 4 November, 2008
Accepted: 21 April, 2009