MICROSTRUCTURE AND PHASE TRANSITIONS INVESTIGATIONS IN THE SYSTEM $SrTiO_3$-$PbLiF_3$

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Perovskite oxides ABO_3 exhibit a wide range of practical applications, the last one being the use in cell capacitors. Their relatively simple structure has allowed the modulation of their dielectric characteristics using various ionic substitutions. Among these materials, strontium titanate ($SrTiO_3$) is well known to be paraelectric with a cubic symmetry at room temperature. At the present day, the solid solution $Ba_{1-x}Sr_xTiO_3$ is of a particular interest for the fabrication of high densities memories (FRAMs). The aim of this study is to investigate the microstructure and the phase transitions in the system $SrTiO_3$ - $PbLiF_3$.

A new solid solution $Sr_{1-x}Pb_x(Ti_{1-x}Li_x)O_{3-3x}F_{3x}$ ($0 \leq x \leq 0.15$) with $NaNbO_3$ structure has been synthesized by firing mixtures of $SrTiO_3$ and $PbLiF_3$ in air at 1223 K and characterized by X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). The lattice parameters of these new compounds are given in Table 1.

Table 1: Lattice parameters (300 K) of $Sr_{1-x}Pb_x(Ti_{1-x}Li_x)O_{3-3x}F_{3x}$ compounds

Specimens	a (Å)	b (Å)	c (Å)	V (Å^3)
$SrTiO_3$	3.907 (2)	–	–	59.639 (2)
$Sr_{0.95}Pb_{0.05}(Ti_{0.95}Li_{0.05})O_{2.85}F_{0.15}$	6.379 (1)	15.609 (3)	6.517 (1)	646.835 (3)
$Sr_{0.90}Pb_{0.10}(Ti_{0.90}Li_{0.10})O_{2.70}F_{0.30}$	6.377 (1)	15.623 (2)	6.521 (1)	648.904 (2)
$Sr_{0.85}Pb_{0.15}(Ti_{0.85}Li_{0.15})O_{2.55}F_{0.45}$	6.373 (2)	15.626 (3)	6.519 (2)	649.200 (4)

Dielectric measurements are performed as a function of temperature (123 K – 473 K) and frequency (20 Hz - 10^5 Hz). The permittivity ε'_r shows no maximum in the temperature range investigated (Figure 1).

Differential Scanning Calorimetry (DSC) analyses are carried out between 300 K and 873K. For each sample, three phenomena which could be ascribed to various structural changes are observed on the DSC curves (Table 2).

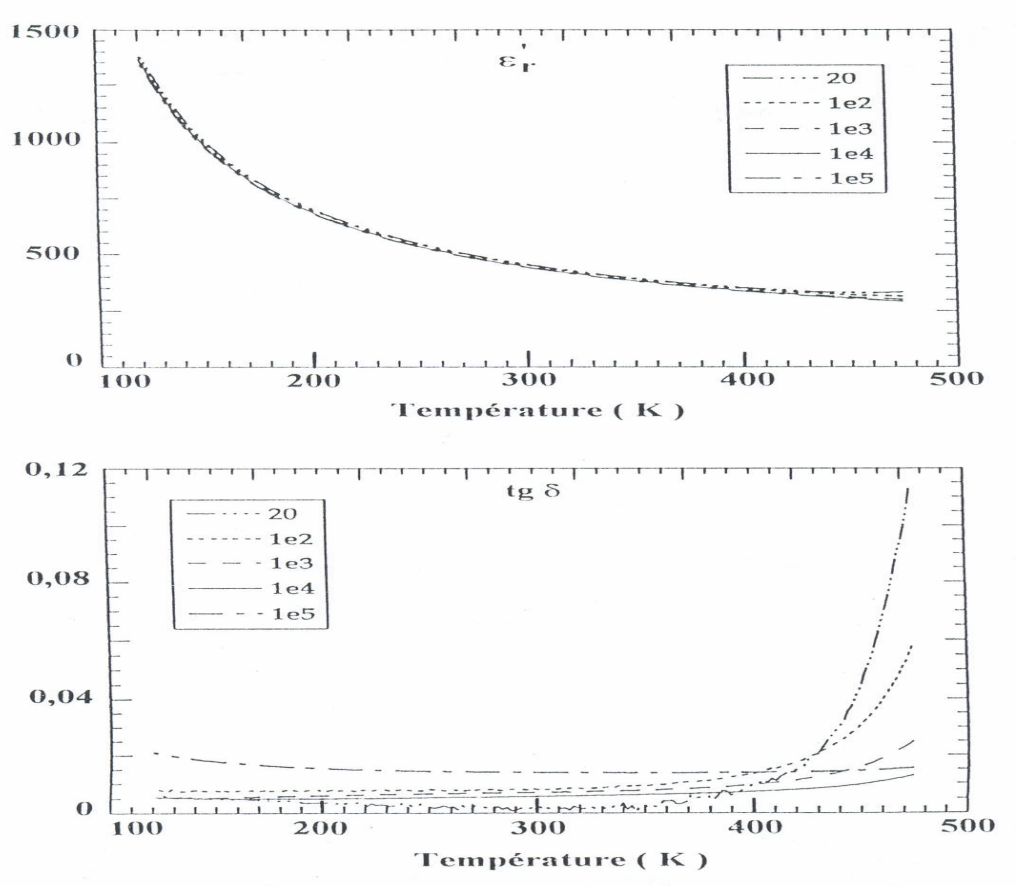

Figure1: Temperature dependence of the permittivity ε'_r and the dielectric losses tan δ for $Sr_{0.97}Pb_{0.03}(Ti_{0.97}Li_{0.03})O_{2.91}F_{0.09}$ ceramic

Table 2: Phase transitions temperatures of $Sr_{1-x}Pb_x(Ti_{1-x}Li_x)O_{3-3x}F_{3x}$ compounds

Specimens	T_1 (K)	T_2 (K)	T_3 (K)
$SrTiO_3$	-	-	-
$Sr_{0.95}Pb_{0.05}(Ti_{0.95}Li_{0.05})O_{2.85}F_{0.15}$	543	669	821
$Sr_{0.90}Pb_{0.10}(Ti_{0.90}Li_{0.10})O_{2.70}F_{0.30}$	537	695	774
$Sr_{0.85}Pb_{0.15}(Ti_{0.85}Li_{0.15})O_{2.55}F_{0.45}$	530	589	750

These phase transitions associated with a small change in heat capacity, are probably of second order (Table 3).

Table 3: Heat capacity of $Sr_{1-x}Pb_x(Ti_{1-x}Li_x)O_{3-3x}F_{3x}$ phases

Phase	Cp (T_1) J mol^{-1} K^{-1}	Cp (T_2) J mol^{-1} K^{-1}	Cp (T_3) J mol^{-1} K^{-1}
$SrTiO_3$	-	-	-
$Sr_{0.95}Pb_{0.05}(Ti_{0.95}Li_{0.05})O_{2.85}F_{0.15}$	18.790	37.579	103.340
$Sr_{0.90}Pb_{0.10}(Ti_{0.90}Li_{0.10})O_{2.70}F_{0.30}$	28.841	1.538	30.764
$Sr_{0.85}Pb_{0.15}(Ti_{0.85}Li_{0.15})O_{2.55}F_{0.45}$	17.895	19.662	53.097