

Influence of Strontium on the Structural and Dielectric Properties of Hydrothermally Processed PbTiO_3 Ceramic

E.H. LAHRAR^{1,*}, O. EL GHADRAOUI¹, A. HARRACH¹, M. ZOUHAIRI³, T. LAMCHARFI² and E.H. EL GHADRAOUI¹

¹Chemistry of Condenser Matter Laboratory, Faculty of Sciences and Technologies, Sidi Mohamed Ben Abdellah University, B.P. 2202, Fez, Morocco

²Signals, Systems and Components Laboratory, Faculty of Sciences and Technologies, Sidi Mohamed Ben Abdellah University, B.P. 2202, Fez, Morocco

³Team of Materials, Membranes and Separation Processes, Faculty of Sciences, Moulay Ismail University of Meknes, Meknes city, Morocco

*Corresponding author: Tel: +212 13 447889; E-mail: lahrarhoucine@gmail.com

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Perovskite ceramic materials of the composition $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ (PS_xT) were prepared by hydrothermal process at a relatively low temperature. The solution of KOH favours the solubility of the precursors in solid state. Pressure and temperature are critical factors for the formation of pure perovskite PS_xT phase. The reaction mixture in stoichiometric amount is put in an autoclave and treated at 180 °C for 24 h. The powder obtained after grinding is treated at 400 °C for 4 h. X-ray diffraction shows that the compounds crystallize in a pure phase of perovskite type. SEM morphology indicates a homogeneous microstructure of the grains with the presence of pores. The impedance spectroscopy study in the frequency range (1 KHz – 2 MHz) confirms the insertion of strontium into the lead titanate matrix and highlights the strontium effect on the transition temperature (T_c) and the value of dielectric permittivity (ϵ_r).

Keywords: Strontium, Lead titanate, Ferroelectric, Hydrothermal process, Dielectric permittivity.

INTRODUCTION

Perovskite materials are highly studied because of their relatively simple structure and the possibility of modifying their physico-chemical characteristics by ionic substitutions at the different sites A and B of the ABO_3 structure. These materials are of great interest due to the existence of a large number of ferroelectric phases. Moreover, these materials are likely to be used in many applications such as microelectronics, FeRAM memories, micro-actuators or displacement sensors because of their high-performance dielectric properties [1-4]. The most studied perovskite-type materials are BaTiO_3 , SrTiO_3 , PbTiO_3 , $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ (PZT) which have given rise to numerous studies concerning their properties, in particular, their ferroelectric characteristics [5-7].

Lead titanate, PbTiO_3 (PT), is a well-known perovskite ferroelectric ceramic. It is characterized by remarkable ferroelectric, piezoelectric and pyroelectric properties [8], having a high Curie temperature ($T_c = 490$ °C) and a low dielectric

constant. It is known that bulk PbTiO_3 has a tetragonal network with a high quadracity (characterized by the ratio c/a , where a and c are network parameters) at room temperature and cubic symmetry at Curie temperature (T_c) [9]. The ferroelectric properties of ABO_3 perovskite materials can be effectively modified and controlled by insertion and/or substitution with different doping elements [10-13].

To date, several researchers have shown great interest in PbTiO_3 optimizing its more effective applications. Doping is of fundamental importance for crystallographic phase control and modification of electronic properties. A variety of different dopants can be introduced into the PbTiO_3 network, Sr^{2+} cation was chosen in this study as an isovalent substituent for Pb^{2+} ions. It aims to improve the physico-chemical properties of the latter. The ionic radius of Sr^{2+} ($r^{2+} = 1.11$ Å) is smaller than that of Pb^{2+} ($r^{2+} = 1.19$ Å) so it can occupy site A. One of the processes used to prepare PbTiO_3 (PT) and $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ ceramics noted that the PST is the hydrothermal process. This method consists of a heat treatment under pressure in an

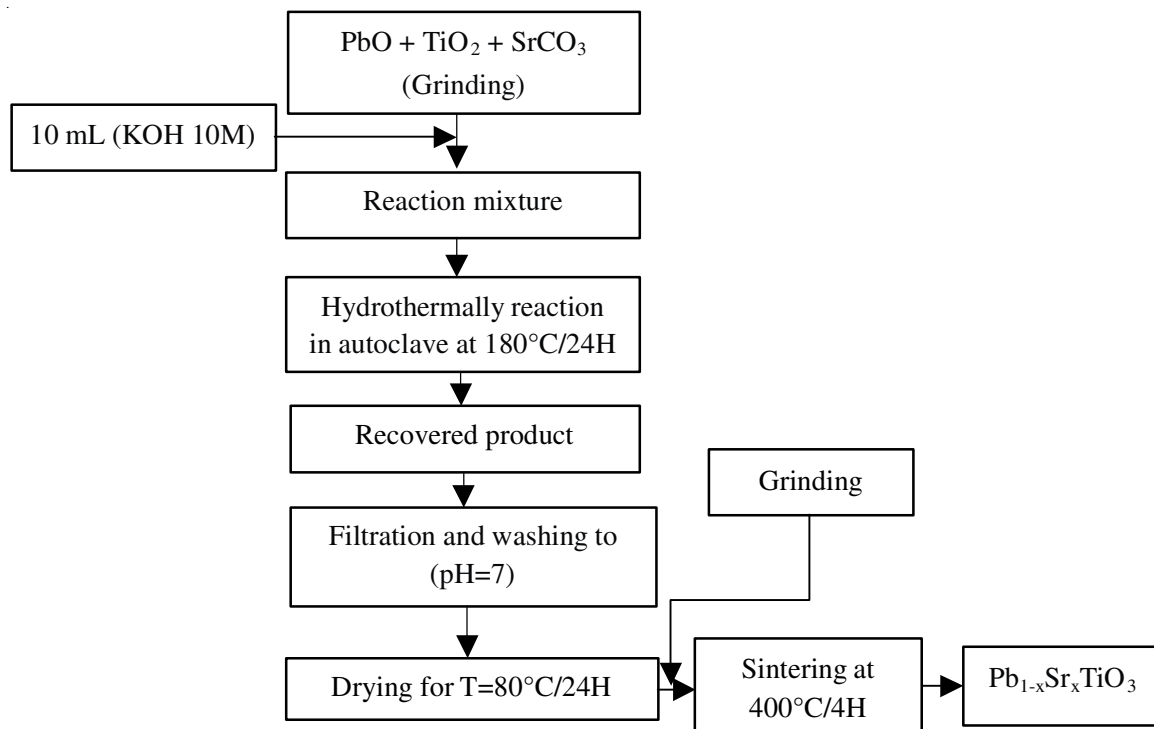


Fig. 1. Synthesis of $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ phase by hydrothermally method

autoclave containing an aqueous solution in a basic medium in the presence of oxides, hydroxides or carbonate [14]. The reaction takes place at a temperature between 100 and 374 °C and the pressure can reach 15 MPa.

This work aims to study the effect of inserting Sr^{2+} into the lead titanate (PbTiO_3) matrix. A series of $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ compositions ($0 \leq x \leq 1$) was synthesized by the hydrothermal route. The powders obtained were characterized by X-ray diffraction, scanning electron microscopy and dielectric measurements. The experimental results show the insertion of strontium into the lead titanate structure and its influence on the different physico-chemical properties of the obtained material.

EXPERIMENTAL

To study the influence of strontium on the physico-chemical properties of lead titanate (PbTiO_3), a series of powders of composition $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ was studied. The synthesis of $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ compounds by the hydrothermal process was carried out in the form of powders from the precursors PbO , SrCO_3 and TiO_2 which were taken in stoichiometric amounts, the mixture was grounded for 1 h in a porcelain mortar. A 10 mL KOH (10 M) was added to these precursors mixed with distilled water. The heterogeneous solution obtained was stirred for 1 h and the mixture was placed in an autoclave filled to 80 % of its volume.

The whole system undergoes a treatment at 180 °C for 24 h, with a rise of 5 °C/min, and a descent to the furnace inertia. The product was washed with distilled water until it is neutral, then dried in an oven (80 °C) for 24 h. The powder obtained was then treated at 400 °C for 4 h. The powders were recovered and undergo another grinding for 30 min. Fig. 1 represents different stages of development of $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ phases by hydrothermal route.

RESULTS AND DISCUSSION

X-ray diffraction (XRD) analysis: Different composition of the solid solution $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ ($0 \leq x \leq 1$) produced by hydrothermal method were characterized by XRD. The spectra obtained are shown in Fig. 2. For $x = 0$, only phase present was that of pure perovskite PbTiO_3 , which crystallizes in the quadratic system of space group $Pm4m$.

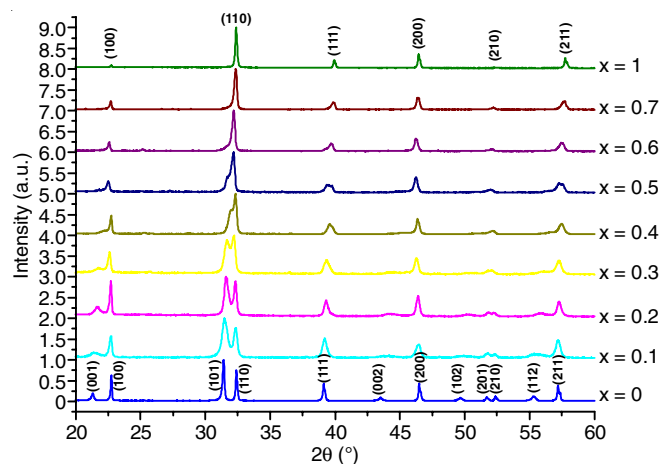


Fig. 2. XRD patterns of $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ ($0 \leq x \leq 1$) synthesized at 180 °C for 24 h and treated at 400 °C for 4 h

The spectra corresponding to strontium rates of $x = 0.1$; 0.2; 0.3 and 0.4, respectively, showed that the phases were indexed in the isotype quadratic symmetry structure of PbTiO_3 . Using a concentration of $x = 0.5$ strontium, a peak splitting disappears when the Sr concentration increases to $x = 0.7$ (Fig. 3), which crystallizes in the pseudo-cubic system. For $x = 1$, obtained spectrum was a characteristic of pure phase of SrTiO_3 , which crystallizes under the cubic system of space group $Pm3m$.

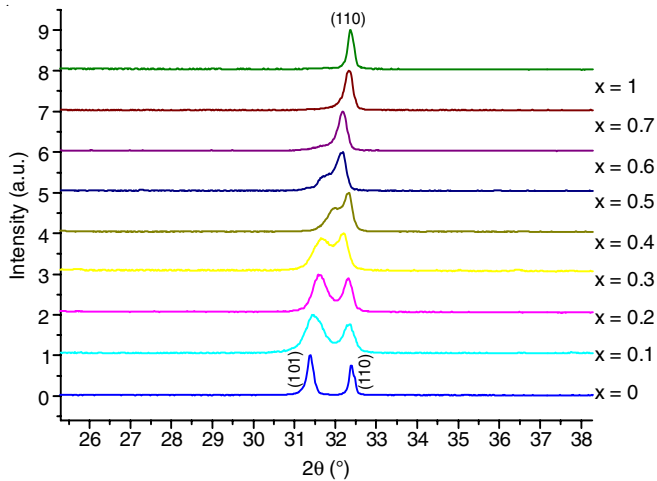


Fig. 3. XRD patterns of the peaks (101) and (110) in the range of $30 \leq 2\theta \leq 34$

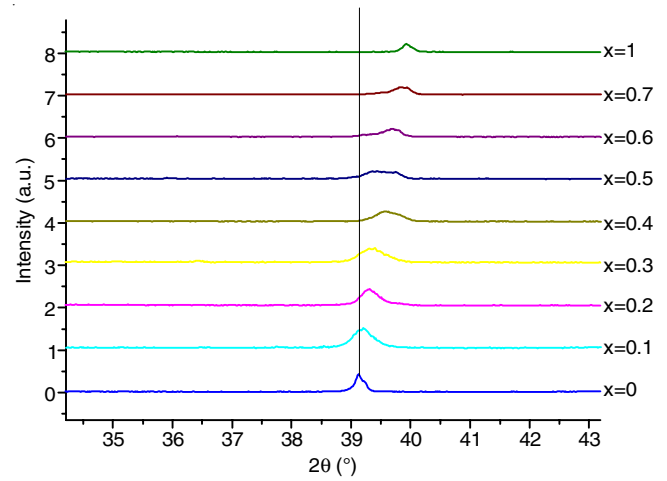


Fig. 4. XRD patterns of the peaks (111) in the range of $38 \leq 2\theta \leq 40$

Fig. 4 shows the peak (111) at the interval of $38^\circ \leq 2\theta \leq 40^\circ$. It was observed that the introduction of Sr causes the shift of this peak to a wide angles, which might be attributed due to the fact that ionic radius of Sr^{2+} (1.11 Å) is smaller than that of Pb^{2+} (1.19 Å). This displacement indicates an incorporation of Sr into the lead titanate (PbTiO_3) structure. We also observed the fusion of two peaks (101) and (110) of the quadratic phase into a single peak (110), which shows the transition from the quadratic phase to the pseudo-cubic phase (Fig. 3).

Doping with strontium, it was observed that the parameter (c/a) decreases with the concentration of Sr increases (Table-1) and reduces tetragonality to a phase transformation from quadratic to pseudo-cubic structure.

Microstructure analysis: Fig. 5 shows the microstructure of $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ samples ($0 \leq x \leq 0.6$) prepared by the hydro-

TABLE-1
PARAMETERS, TETragonALITY c/a AND CELL VOLUME FOR $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ PREPARED BY HYDROTHERMAL PROCESS

| $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ | $a = b$ (Å) | c (Å) | c/a | Cell volume (Å ³) |
|--|-------------|---------|------------|-------------------------------|
| X = 0.0 | 3.9042 | 4.1584 | 1.06510937 | 63.3855665 |
| X = 0.1 | 3.9100 | 4.1249 | 1.05496164 | 63.0618837 |
| X = 0.2 | 3.9193 | 4.0949 | 1.04480392 | 62.9014006 |
| X = 0.3 | 3.9242 | 4.0400 | 1.02950920 | 62.2133564 |
| X = 0.4 | 3.9268 | 3.9920 | 1.01660385 | 61.5556749 |
| X = 0.5 | 3.9270 | 3.9602 | 1.00845429 | 61.0715471 |
| X = 0.6 | 3.9250 | 3.9449 | 1.00507006 | 60.7736501 |
| X = 0.7 | 3.9200 | 3.9234 | 1.00086735 | 60.2885338 |
| X = 1.0 | 3.9200 | 3.9200 | 1.00000000 | 60.2362880 |

thermal process, sintered at 1000 °C for 4h. It shows that the texture of the materials was uniform, as well as the grains

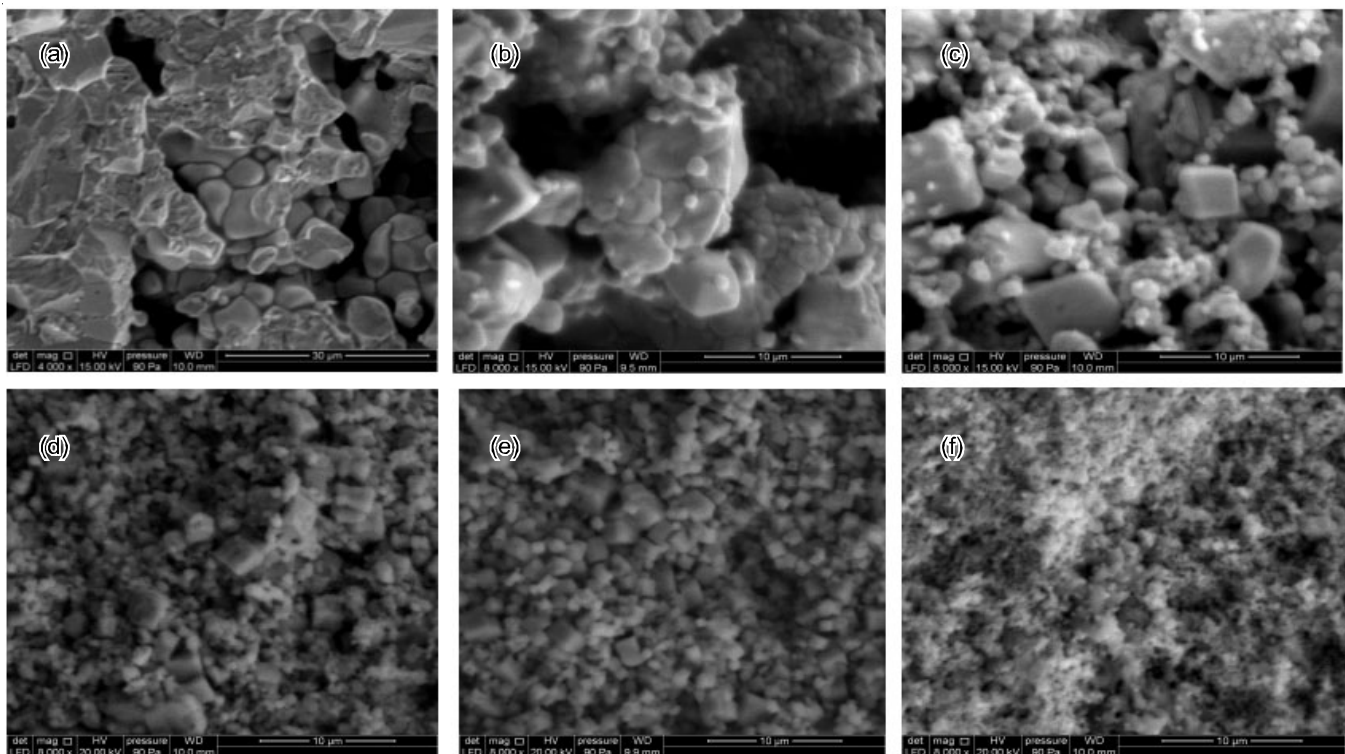


Fig. 5. Microstructure of $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ ($x = 0, 0.1, 0.2, 0.3, 0.5$ and 0.6) synthesized by hydrothermal process

were distributed however, their size varies with Sr concentration. The average grain size for sample $x = 0.1$ varies approximately $4.885 \mu\text{m}$ and $0.49 \mu\text{m}$ for sample $x = 0.6$. This can be interpreted by the fact that substitution of Pb^{2+} ions by Sr^{2+} decreases the value of mesh parameters and therefore the volume of crystal structure and the size of grains. This analysis confirms the results obtained by XRD.

Dielectric properties: Fig. 6 shows the evolution of permittivity as a function of temperature at different frequencies (1 KHz – 2 MHz) for $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ compositions. The maximum dielectric permittivity (ϵ_r) is frequency independent. It thus passes through a ferroelectric phase transition which is polar to the a polar para-electrical phase with an increase in permittivity. Above 40% strontium, the permittivity undergoes a rapid fall, which might be due to the relaxing character of strontium having vacant sites. It is also observed that the transition temperature (T_c) remains constant for different doping rates as a function of frequency (Table-2), which shows that a classic ferroelectric material is obtained.

Diffuse transition: Fig. 7 shows the linear adjustment of dielectric behaviour, studied using modified Uchino's law to

TABLE-2
VALUES OF DIELECTRIC PERMITTIVITY (ϵ_r) AND CURIE TEMPERATURE (T_c) OF $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ PELLETS ($0 \leq x \leq 0.6$) FOR A FREQUENCY OF 2 MHz

| x | T_c (°C) | ϵ_r |
|-----|------------|--------------|
| 0.1 | 456.000 | 771.860 |
| 0.2 | 384.296 | 807.540 |
| 0.3 | 310.000 | 852.607 |
| 0.4 | 250.640 | 1309.125 |
| 0.5 | 109.400 | 212.746 |
| 0.6 | 62.7600 | 189.578 |

determine the parameters γ and δ which respectively define the diffuse nature of transition and relaxer [15].

$$\ln\left(\frac{\epsilon_{\max}}{\epsilon_r} - 1\right) = \gamma \ln(T - T_m) - \gamma \ln(2\delta)$$

where γ and δ are the relaxor and diffuse parameters, respectively.

The experimental points line up well on a straight line. This shows that these compounds follow this modified puissance law, whose theoretical approach allows the determination of

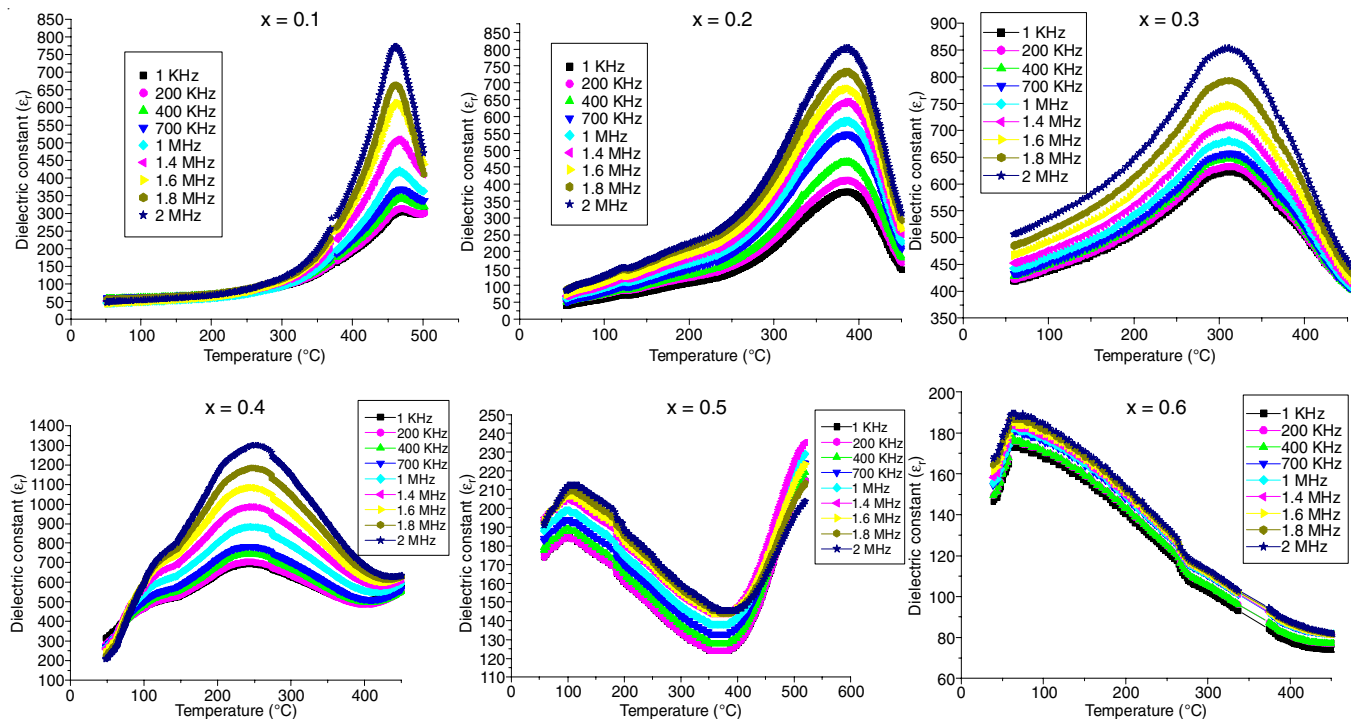


Fig. 6. Thermal variation of relative permittivity (ϵ_r) of $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ ($x = 0.1, 0.2, 0.3, 0.4, 0.5$ and 0.6) heat treated at $1000 \text{ }^\circ\text{C}$ for 4 h

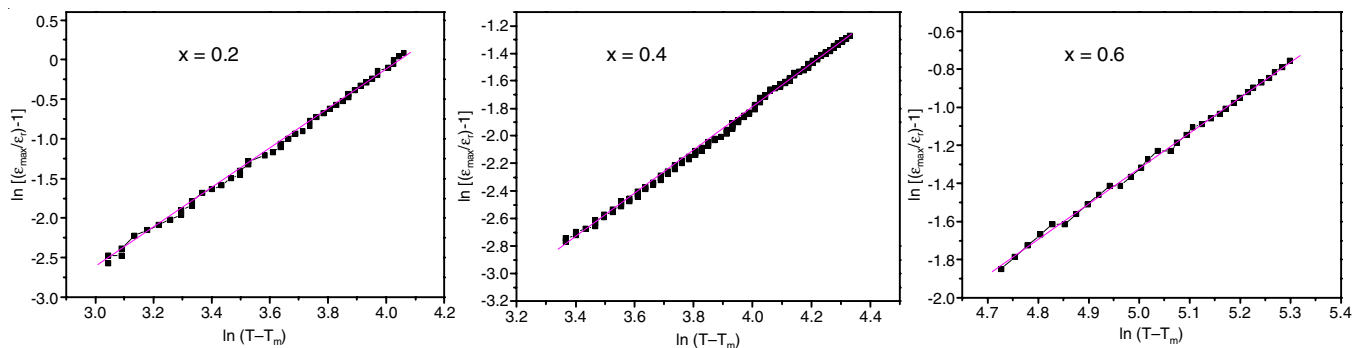


Fig. 7. Evolution of $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ using Uchino's law ($x = 0.2, 0.4$ and 0.6) in the paraelectric domain ($T > T_c$) at 1 KHz

the coefficient γ which measures the degree of deviation of thermal behaviour compared to the standard Curie-Weiss law. The values γ and δ are given in Table-3. These values increase with increasing amounts of inserted strontium. Indeed, the evolution of these constants shows that transition was becoming more diffuse ($1 < \gamma < 2$). The diffuse behaviour of the curie transition is considered to result from the inter-crystalline constraints that occur when the atomic order was absent within the material [16].

TABLE-3
Pb_{1-x}Sr_xTiO₃ PARAMETER VALUES (γ , δ)
FOR A FREQUENCY OF 1 KHz

| Strontium (%) | γ | δ |
|---------------|----------|----------|
| 10 | 1.381 | 36.56 |
| 20 | 1.411 | 37.01 |
| 30 | 1.489 | 46.12 |
| 40 | 1.572 | 47.45 |
| 50 | 1.577 | 49.09 |
| 60 | 1.689 | 51.76 |

Conclusion

A perovskite ceramic materials Pb_{1-x}Sr_xTiO₃ ($0 \leq x \leq 1$) were prepared by hydrothermal process. XRD analysis of these powders showed that they crystallize in the perovskite phase of quadratic symmetry ($0 \leq x \leq 0.5$), at 60 % Sr content there is a transition from the quadratic phase to the pseudo-cubic phase. SEM images showed that strontium doping decreases grain size and affects their shapes. Dielectric measurements performed on these compounds indicated the insertion of Sr into the Pb_{1-x}Sr_xTiO₃ matrix decreases the transition temperature T_c and increases the dielectric permittivity (ϵ_r), thus a diffuse character of ferro to paraelectric transition.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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