Influence of Strontium on the Structural and Dielectric Properties of Hydrothermally Processed PbTiO₃ Ceramic

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Perovskite ceramic materials of the composition $Pb_{1-x}Sr_xTiO_3$ (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 ºC for 24 h. The powder obtained after grinding is treated at 400 ºC 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 stronium 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 ABO₃ 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 BaTiO₃, SrTiO₃, PbTiO₃, PbZr$_x$Ti$_{1-x}$O₃ (PZT) which have given rise to numerous studies concerning their properties, in particular, their ferroelectric characteristics [5-7].

Lead titanate, PbTiO₃ (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 ºC) and a low dielectric constant. It is known that bulk PbTiO₃ 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 ABO₃ 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 PbTiO₃ 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 PbTiO₃ network, Sr²⁺ cation was chosen in this study as an isovalent substituent for Pb²⁺ ions. It aims to improve the physico-chemical properties of the latter. The ionic radius of Sr²⁺ (r²⁺ = 1.11 Å) is smaller than that of Pb²⁺ (r²⁺ = 1.19 Å) so it can occupy site A. One of the processes used to prepare PbTiO₃ (PT) and Pb$_{1-x}$Sr$_x$TiO₃ ceramics noted that the PST is the hydrothermal process. This method consists of a heat treatment under pressure in an

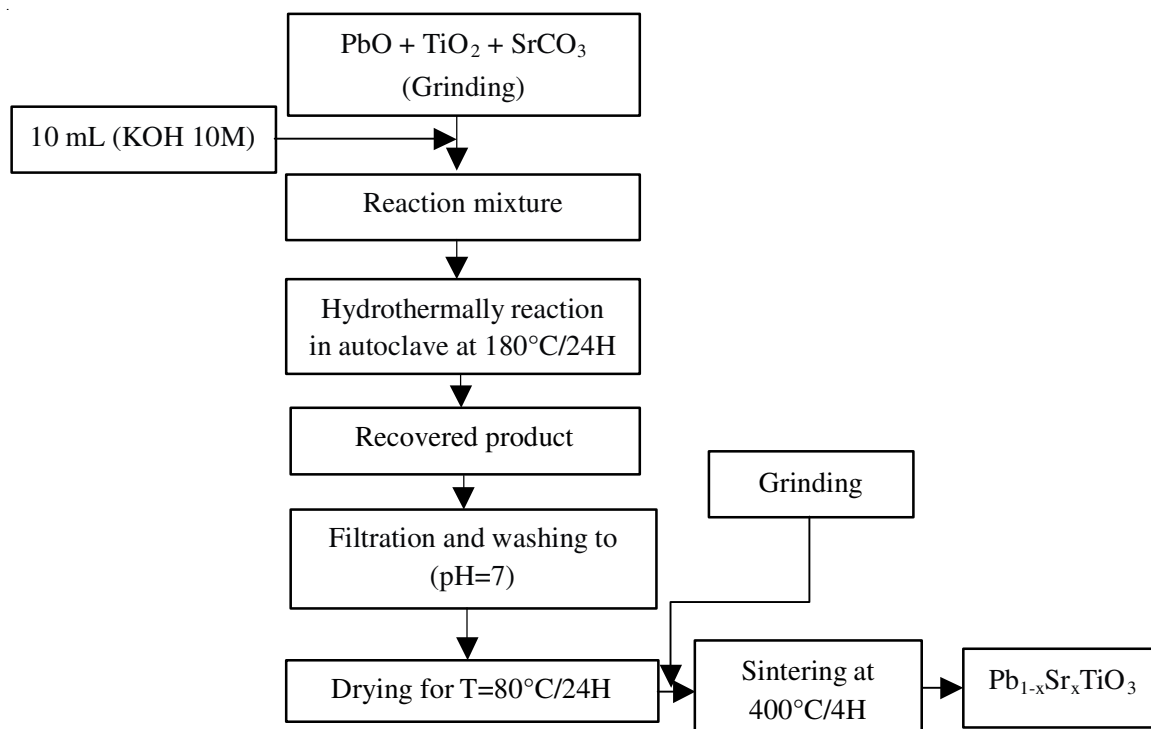Fig. 1. Synthesis of $Pb_{1-x}Sr_xTiO_3$ phase by hydrothermally method

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 ºC 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 $Pb_{1-x}Sr_xTiO_3$ 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 $Pb_{1-x}Sr_xTiO_3$ was studied. The synthesis of $Pb_{1-x}Sr_xTiO_3$ 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 ºC for 24 h, with a rise of 5 ºC/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 ºC) for 24 h. The powder obtained was then treated at 400 ºC for 4 h. The powders were recovered and undergo another grinding for 30 min. Fig. 1 represents different stages of development of $Pb_{1-x}Sr_xTiO_3$ phases by hydrothermal route.

RESULTS AND DISCUSSION

X-ray diffraction (XRD) analysis: Different composition of the solid solution $Pb_{1-x}Sr_xTiO_3$ ($0 \leq x \leq 1$) 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 P*m4m*.

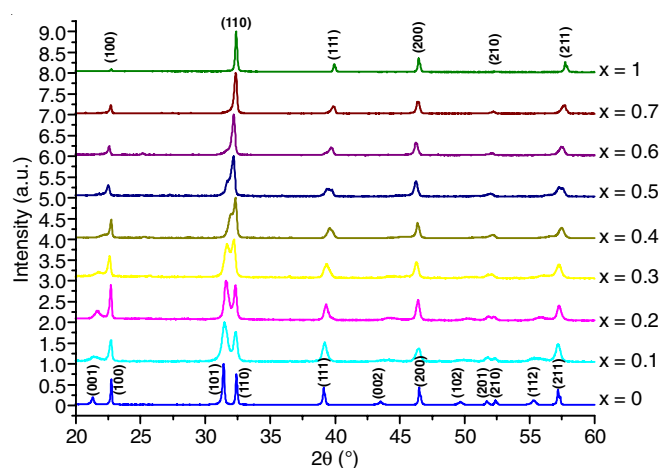Fig. 2. XRD patterns of $Pb_{1-x}Sr_xTiO_3$ ($0 \leq x \leq 1$) synthesized at 180 °C for 24 h and treated at 400 °C for 4 h

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 P*m3m*.
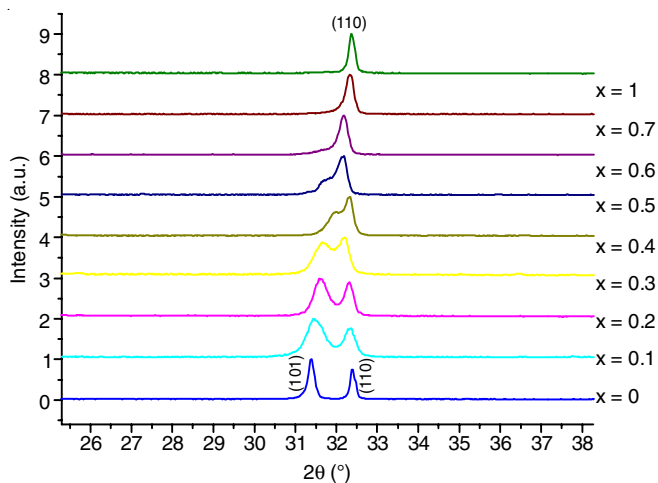
Fig. 3.   XRD patterns of the peaks (101) and (110) in the range of $30 \le 2\theta \le 34$

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

Fig. 4 shows the peak (111) at the interval of $38° \le 2\theta \le 40°$. 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 $Pb_{1-x}Sr_xTiO_3$ samples ($0 \le x \le 0.6$) prepared by the hydro-

TABLE-1
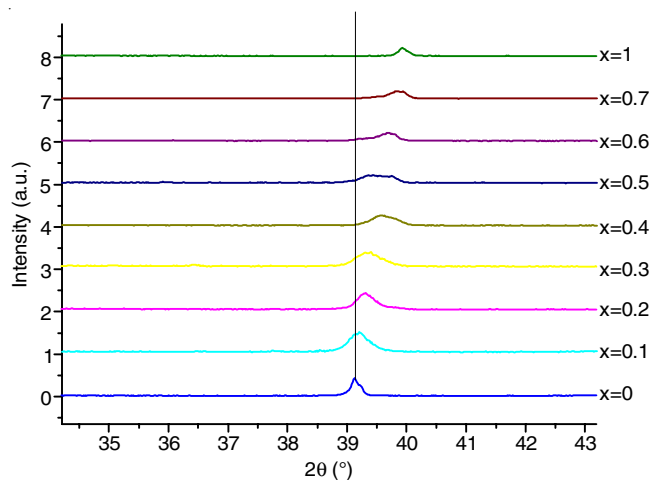PARAMETERS, TETRAGONALITY c/a AND CELL VOLUME
FOR $Pb_{1-x}Sr_xTiO_3$ PREPARED BY HYDROTHERMAL PROCESS

$Pb_{1-x}Sr_xTiO_3$	a = b (Å)	c (Å)	c/a	Cell volume (Å³)
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
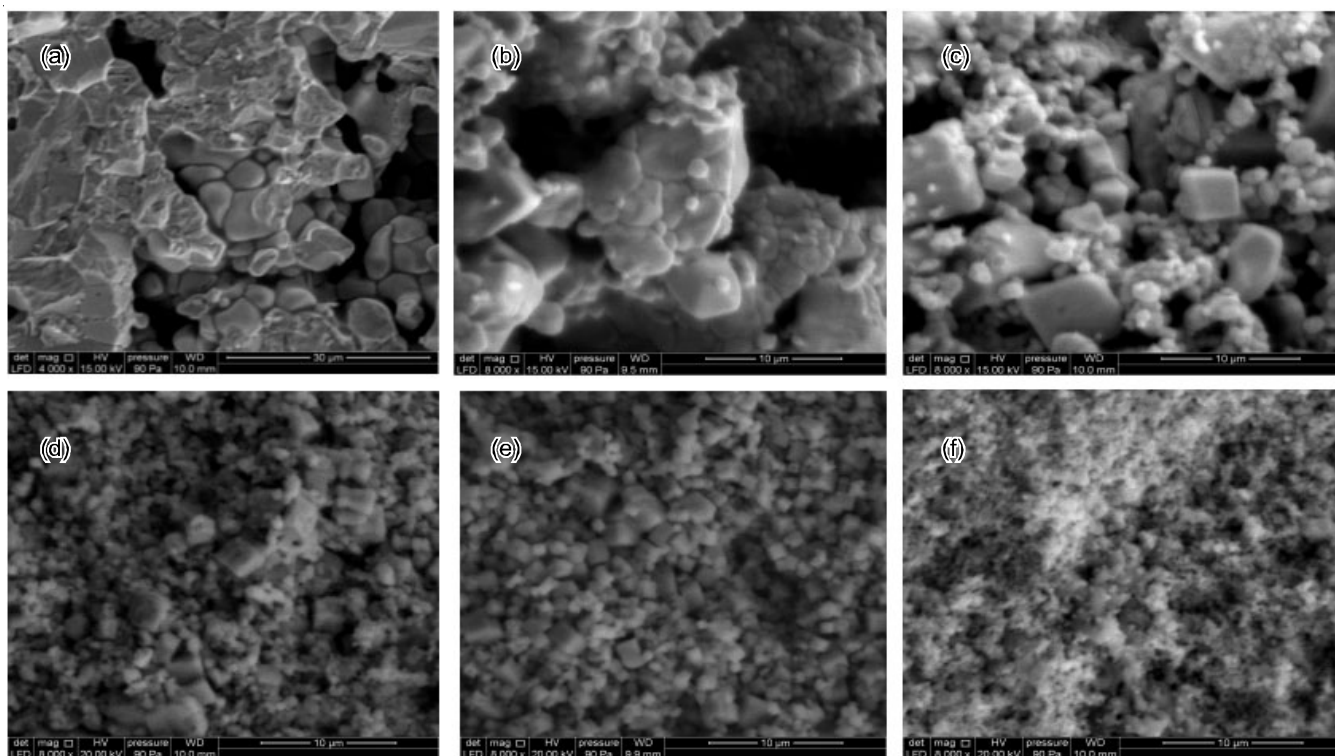

Fig. 5. Microstructure of $Pb_{1-x}Sr_xTiO_3$ (x = 0, 0.1, 0.2, 0.3, 0.5 and 0.6) synthesized by hydrothermal process

were distributed however, their size varies with Sr concentration. The average grain size for sample x = 0.1 varies approximately 4.885 μm and 0.49 μm for sample x = 0.6. This can be interpreted by the fact that substitution of Pb²⁺ ions by Sr²⁺ 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 Pb₁₋ₓSrₓTiO₃ 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 Pb₁₋ₓSrₓTiO₃ PELLETS
($0 \le x \le 0.6$) 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].

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

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
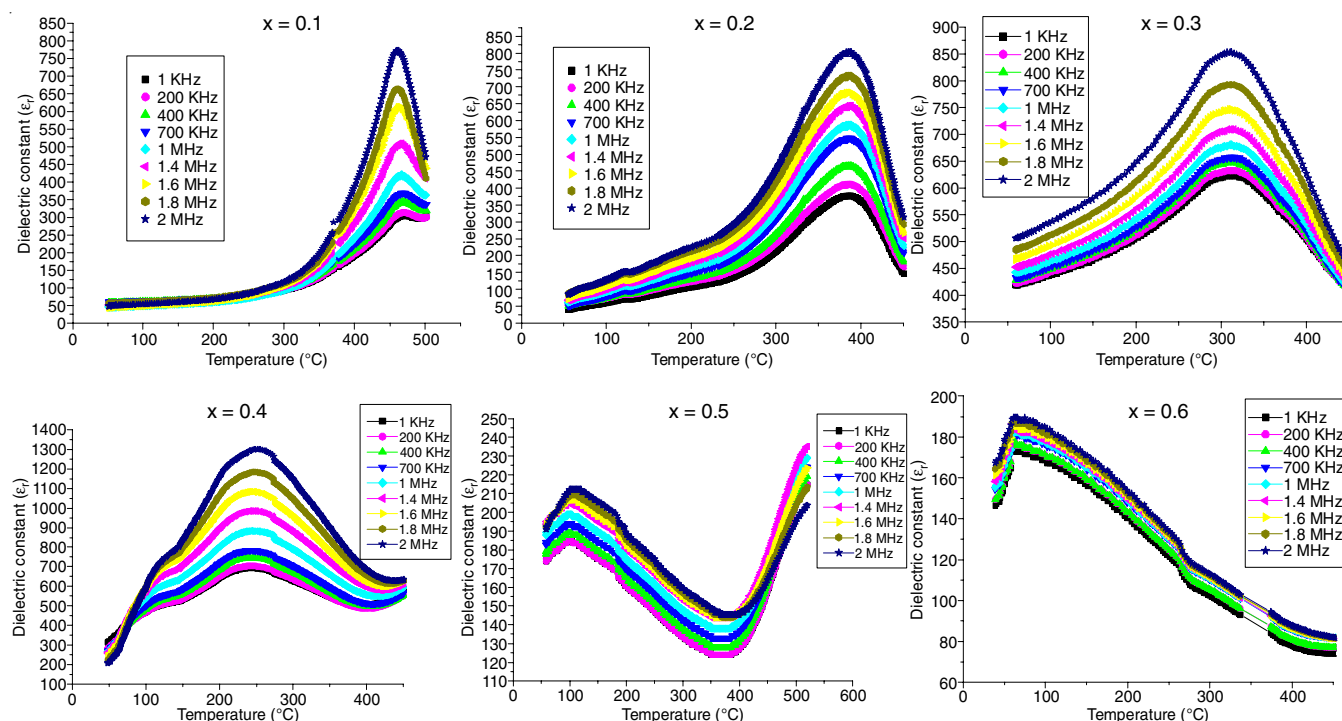

Fig. 6. Thermal variation of relative permittivity (ε_r) of Pb₁₋ₓSrₓTiO₃ (x = 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6) heat treated at 1000 °C for 4 h
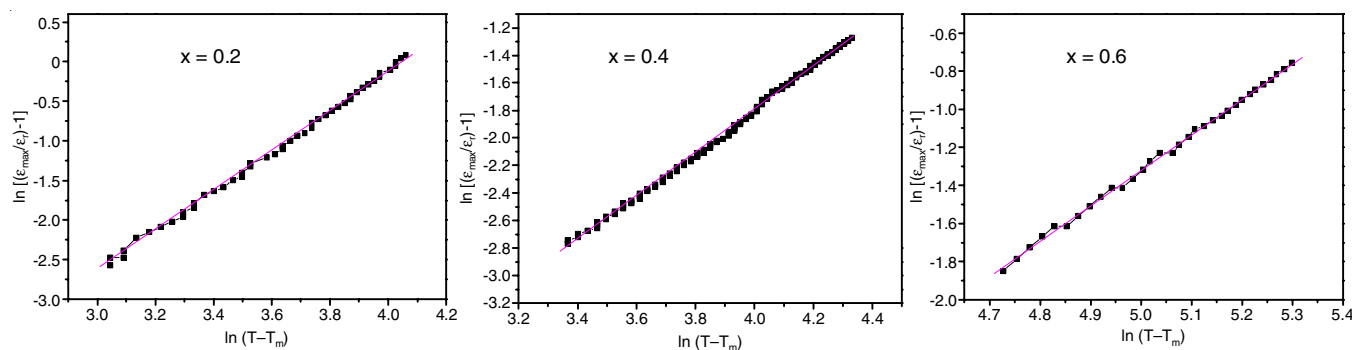
Fig. 7. Evolution of Pb₁₋ₓSrₓTiO₃ using Uchino's law (x = 0.2, 0.4 and 0.6) in the paraelectric domain (T > T_c) at 1 KHz

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 ($1 < γ < 2$). 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$_x$TiO$_3$ 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$_x$TiO$_3$ ($0 ≤ x ≤ 1$) were prepared by hydrothermal process. XRD analysis of these powders showed that they crystallize in the perovskite phase of quadratic symmetry ($0 ≤ x ≤ 0.5$), 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$_x$TiO$_3$ 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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