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Research Article **PHYSICS**

Investigating the Structural and Dielectric Properties of La-doped $PbLa_xTi_{(1-3/4x)}O_3$ Perovskite Ceramics: The Role of La Content

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KEY WORDS

Perovskite structure, Lead titanate, La-ions, Ferroelectric materials

ABSTRACT

In this study, $PbLa_xTi_{(1 - 3/4 x)}O_3$ (PLT) ceramics were prepared using the tartrate precursor method with varying La content (x= 0, 0.04, and 0.1). The samples were annealed at 600°C and characterized using X-ray diffraction, Fourier-transform infrared spectroscopy, high-resolution transmission electron microscopy and dielectric measurements. The results showed that all samples doped with La ions had a first-order structural phase transition from tetragonal to cubic at the Curie temperature (Tc). This phase transition was also associated with a transition from ferroelectric to paraelectric phase. The dielectric spectra revealed that the material displayed relaxer-type ferroelectric behavior, with Tc shifting to a higher value and dielectric constant increasing with increasing La content up to x= 0.04. The increase in dielectric constant was attributed to the decrease in grain size in the given range of La content. Furthermore, La doping in lead titanate (PT) led to the formation of A-site vacancies, which affected the Curie temperature and the atomic radius between La and Pb ions. This study highlights the potential of using La ions as a dopant in PT ceramics to improve their ferroelectric properties, specifically by inducing a relaxor behavior.

Introduction

In recent years, ferroelectric materials have gained significant attention in the field of electrical and optoelectronic devices due to their unique properties. These materials have a wide range of applications in dielectric capacitors, optical devices, piezoelectric filters, pyroelectric detectors, and acoustic transducers **(Pinto *et al.*, 2010).** Among the most promising a ferroelectric material is lead lanthanum titanate (PLT), also known as lanthanum (La) modified lead titanate, which has a perovskite structure ABO_3. The incorporation of La into $PbTiO_3$ leads to changes in the physical properties of the material, such as increased permittivity and reduced tetragonality **(Fe, 2019; Tawfik *et al.*, 2018).**

The use of nanoscale particles in the synthesis of ferroelectric materials has gained increasing attention in recent years, as it has been shown that these particles exhibit distinct properties compared to their bulk counterparts. Various synthetic methods, such as the hydrothermal process, sol-gel processing and tartrate precursor method, have been developed to produce a wide range of compounds at the nanometric scale. One of the most widely used doping agents in ferroelectric materials is lanthanum (La), which is known to have a profound effect on the properties of perovskite-structured compounds. La doping at the A-sites of lead titanate (PT) results in a reduction of tetragonality **(Kongtaweelert *et al.*, 2004),** an increase in permittivity and transition temperature (Tc), and a broadening of the Curie point temperature **(Gao *et al.*, 2016).** These modified materials have a wide range of potential applications in fields such as dynamic random-access memory, electro-optic and actuator systems. However, their most significant application is in pyroelectric infrared sensors, particularly for high frequency applications **(Lakouader *et al.*, 2022; Hemeda *et al.*, 2019a; Tavares *et al.*, 1998; Vaseashta *et al.*, 2022).**

The aim of the work was investigating the synthesis of PLT using the tartrate precursor method. The samples were prepared with different La content (x= 0, 0.04, and 0.1) and were characterized by a combination of analytical techniques, including X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), high-resolution transmission electron microscopy (TEM) and dielectric study with temperature. Our

results indicate that the incorporation of La ions into $PbTiO_3$ leads to a change in the structural attributes of the lead titanate and a shift in the Curie temperature. Additionally, we observed an increase in the dielectric constant and a reduction in tetragonality as the La content increased. Overall, this study provides a deeper understanding of the relationship between the structural attributes of PLT and the La concentration, and highlights the potential of using this material in various electrical and optoelectronic devices **(Mallick *et al.*, 2022).**

Materials and method

The powders of $PbLa_xTi_{(1 - 3/4\ x)}O_3$, where x is 0, 0.04, and 0.1, were prepared using the tartrate precursor method. The materials used were titanium dioxide (TiO_3), tartaric acid ($C_4H_6O_6$), lead nitrate ($Pb(NO_3)_2$) with 99% purity, and lanthanum nitrate ($La(NO_3)_3.6H_2O$) with 98% purity. The chemicals were weighed in a stoichiometric ratio and mixed with 250ml of distilled water. The mixture was heated on a magnetic stirrer at 80°C until dry, and then dried at 100°C overnight. The powder was collected and annealed at 600°C for 2 hours. It was then pressed into tablets using a compressor at 5MPa. The crystallite size of the prepared samples was measured using X-ray diffraction (XRD) with a Philips model (PW-1729) diffractometer using a wavelength of 1.540598 Å in the 2θ range of 20 to 80°. Fourier-transform infrared spectroscopy (FTIR) was used to analyze the samples with a Perkin Elmer model 1430 at room temperature in the range of 200 to 4000cm^{-1} in (Egypt, Tanta University, Central lab). The morphology of the prepared samples was characterized by the particle size, which was obtained using transmission electron microscopy (TEM) with a JEOL model 1010 in (National research Center, Cairo, Egypt). The dielectric constant (ε) of the produced samples at various temperatures was measured using an RLC bridge of type BM591 (Solid Lab, Tanta university, Egypt).

Results and discussion

X-ray diffraction analysis (XRD):

X-ray diffraction (XRD) patterns were obtained for $PbLa_xTi_{(1 - 3/4\ x)}O_3$ ceramics (PLT) with various La contents (x=0, 0.04, and 0.1) to examine the crystal structure of the samples. The XRD patterns **Fig. (1)**, indicate that all samples exhibit a tetragonal perovskite phase, as seen in the peak at 2θ = 31° with indices (101). However, for sample x= 0.1, a reduction in the tetragonal phase is observed and a new phase, designated as α-PbO, appears with a

peak at 2θ = 26°. This new phase is likely to be caused by the substitution of La ions for Pb ions in the $PbTiO_3$ lattice, which leads to the formation of a new phase. Additionally, this substitution causes a decrease in the tetragonality factor c/a as the La content increases, except for sample x= 0.1 where a transformation from tetragonal to cubic phase is observed. The disappearance of splitting of the peak (101) at x = 0.1 may be due to the transformation from tetragonal to cubic phase. This result highlights the effectiveness of incorporating La ions into the lead titanate matrix through the tartrate precursor method. Furthermore, Scherrer's equation

$$D = \frac{k\lambda}{\beta \cos\theta} \qquad (1)$$

is used to determine the crystallite size (D) of materials, where λ is the X-ray wavelength for Cu-K radiation, β is the full is the full width at half maximum of the peak, and k is the diffraction peak position was utilized to calculate the crystallite size of the samples and it was found that the crystallite size decreases from 24 nm for x = 0 to 19 nm at x = 0.04 and then increases to 47 nm at x = 0.1 which is correlated to the solubility limit of La ions in the PT phase.

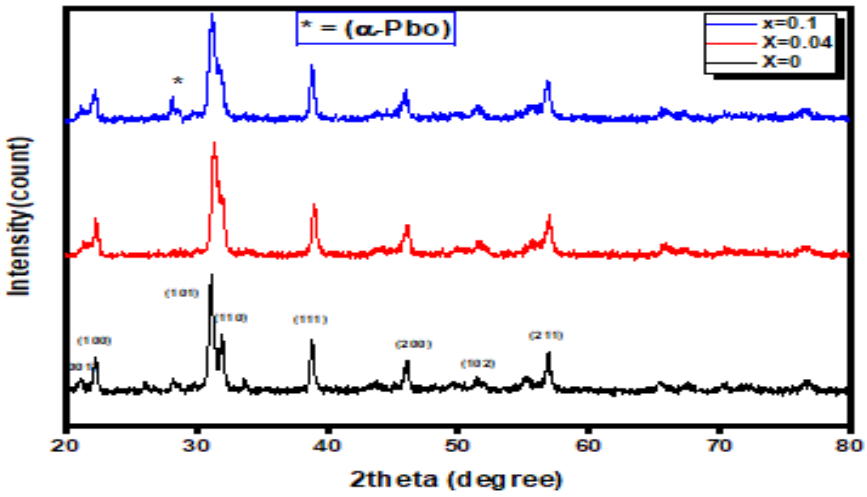

Fig. (1): XRD diffraction patterns for $PbLa_xTi_{(1-3/4x)}O_3$ where (x= 0 ,0.04 and 0.1)

Fourier-transform infrared spectroscopy (FTIR):

In the FTIR spectra of Pb $La_xTi_{(1-3/4\ x)}O_3$ PLT for various La contents (x= 0, 0.04 and 0.1), two major absorption bands are observed at around 360 and 590cm^{-1} **(Hemeda *et al.*, 2021)**, as seen in **Fig.(2)**. These bands are characterized by the stretching and bending vibrational modes of the Ti-O bond, respectively **(Filipič *et al.*, 2016).** Additionally, there is an extra peak at around 1416cm^{-1}, which is attributed to the symmetrical H-O-H vibration **(Hemeda *et al.*, 2019a)**. The O-C-O stretching vibrational mode can also be observed at around 1654cm^{-1} **(Tawfik *et al.*, 2018; Huili *et al.*, 2019).** As the La content increases up to x= 0.04, the absorption band increases before decreasing. In addition, the broad band at about 3400cm^{-1} is for the O-H vibration of water absorbed in the samples. The vibrational modes of the CH_3 and CH_2 symmetry can be identified at 2357cm^{-1}, 2864cm^{-1} and 2924cm^{-1} respectively. Overall, the FTIR spectra confirm the formation of perovskite $PbLaTiO_3$ with a tetragonal structure.

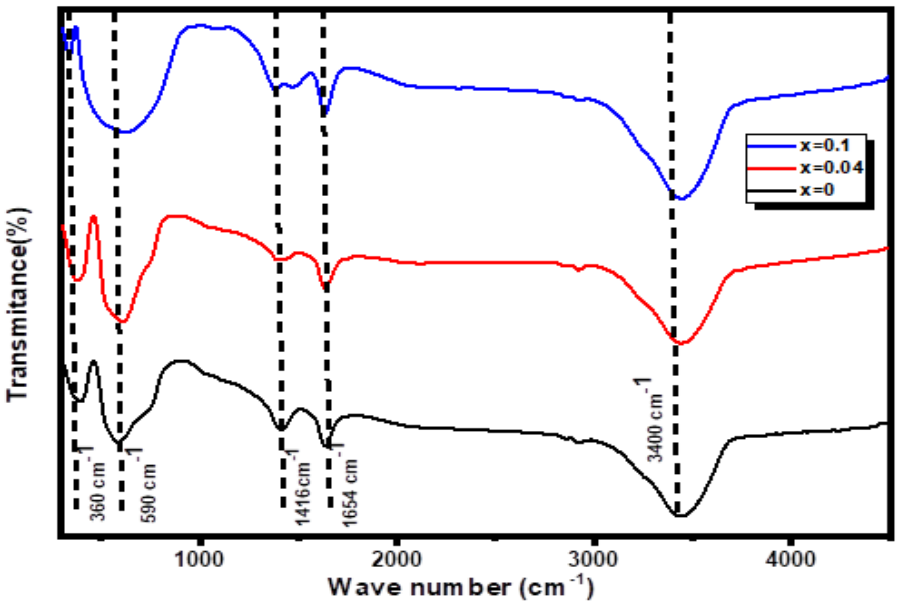

Fig. (2): FTIR spectrum for $PbTiO_3$ doped with La ions at various levels of La content, where (x= 0, 0.04 and 0.1).

High-resolution transmission electron microscopy (TEM)

The TEM images in **Fig. (3)** depict the nano-crystalline structure of $PbTiO_3$ doped with La ions for various concentrations (x= 0, 0.04, and 0.1) synthesized via the tartaric precursor method. The images reveal an average particle size between (36 – 70) nm with some degree of agglomeration. The TEM images also show that at low levels of La doping, a tetragonal crystalline structure is present, while at high levels of La doping, a cubic crystalline structure can be observed. These findings are consistent with the XRD results, which also show that tetragonal crystallization is dominant at low levels of La doping and cubic crystallization is present at high levels of La doping **(Mostafa *et al.*, 2020).**

Dielectric constant (ε) and dielectric loss (tan (δ)): The temperature dependence of the dielectric constant (ε) and dielectric loss (tan δ) of $PbLa_xTi_{(1-3/4x)}O_3$ ceramics, where x = (0, 0.04 and 0.1), were studied as a function of La content using a frequency of 100 KHz. Figs (4,5) illustrates the results of these measurements, where it can be seen that samples doped with La ions undergo a first-order structural phase transition from tetragonal to cubic, accompanied by a transition from ferroelectric to paraelectric phase. The data suggest that the materials exhibit a relaxor behavior up to a La content of x= 0.04, before becoming non-relaxor at x= 0.1 as the structure of the samples changes from tetragonal to cubic.

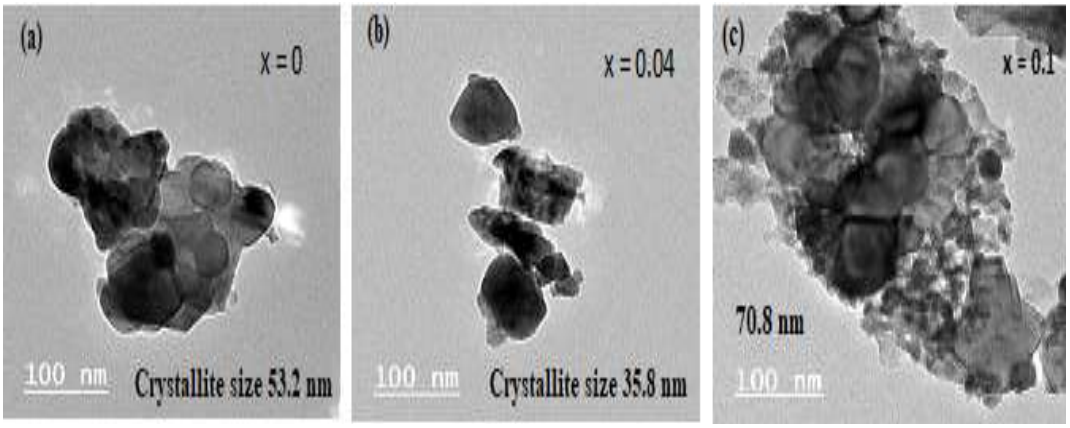

Fig. (3): TEM of ($Pb\ La_xTi_{(1-3/4x)}O_3$), **a)** x = 0, **B)** x = 0.04,and **c)** x = 0.1

As a result, Tc is shifted to higher temperatures and the dielectric constant (ε) increases with increasing La concentration **(Soon *et al*. 2004; Khazanchi *et al.*, 2005**). Up to Tc, the dielectric constant displays a rise with temperature before abruptly decreasing **(Neves *et al.*, 2004; Rayssi *et al.*, 2018).** It is also observed that an increase in crystallite size leads to a decrease in the dielectric constant, indicating the influence of microstructure on dielectric properties. The increase in the dielectric constant near Tc is attributed to the thermal activation of electron hopping between La ions, which leads to local polarization. Above Tc, the material enters a paraelectric state with low polarization, resulting in a decrease in the dielectric constant. Near Tc, the dissipation factor drops sharply as temperature becomes fixed and independent of temperature variation **(Yadav *et al.*, 2020; Kellati *et al.*, 2004).** The structural phase transition and the first-order ferroelectric to paraelectric phase transition have a significant impact on the dissipation factor **(Hemeda *et al.*, 2019b; Assar *et al.*, 2014; Hemeda *et al.*, 2009).**

Additionally, it is noted that increasing La concentration results in decreasing crystallite size leads to an increase in the dissipation factor as in table (1). This is corroborated by the effect of La doping on the Curie temperature of $PLTO_3$, which is shown in **Fig. (4)** and shows a nearly linear reduction in Curie temperature with increasing La doping levels in PTO_3. It is noted that raising the La concentration causes the samples' resistivity to rise, whilst decreasing the crystallite size causes the La content to raise the dissipation factor. When La ions are present, Tc is shifted to a higher temperature and the by increasing Ti, the increase in conductivity may be caused by an increase in dielectric loss **Fig. (5)**.

Table (1): Dielectric constant (ε) variation with temperature and crystallite size (D) as a function of La content from the X-ray

La content	ε (Ω.cm)	XRD crystallite size (D) (nm)
X= 0	15	24
X= 0.04	36.8	19
X= 0.1	12.8	47

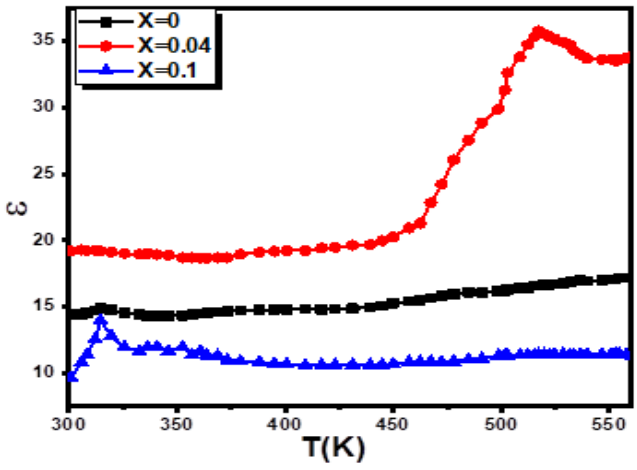

Fig. (4): Dielectric constant variation with temperature at frequency 100KHz for $PbLa_xTi_{(1-3/4x)}O_3$ where (x= 0 ,0.04 and 0.1)

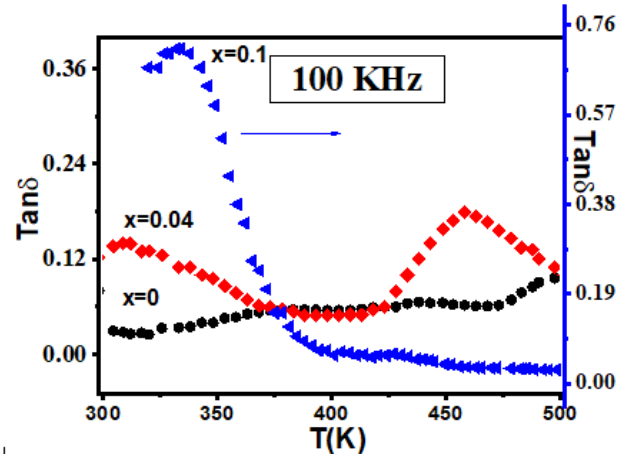

Fig. (5): Dielectric Loss variation with temperature at frequency constant 100KHz for $PbLa_xTi_{(1-3/4x)}O_3$ where (x= 0 ,0.04 and 0.1)

Conclusion

In conclusion, the samples of $PbLa_xTi_{(1-3/4x)}O_3$ ceramics of perovskite type were successfully prepared by using the tartrate precursor method with different La content of x = 0, 0.04, and 0.1. All samples were annealed at 600°C and analyzed by various techniques such as X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), high-resolution transmission electron microscopy (TEM) and dielectric study. The XRD patterns found a tetragonal perovskite structure at the main peak (101) at 2θ near to 31° and the samples x = 0.08 and 0.1 secondary phase. There is a transformation from a tetragonal to cubic phase at sample 0.1. FTIR spectrum shows two main absorption bonds at around 360 cm^{-1} and 590 cm^{-1}. TEM micrographs are in line with the results obtained from XRD. The dielectric constant measured using an RLC bridge shows that up Tc, the dielectric constant displays a rise with rising temperature before abruptly decreasing. This study confirms the efficiency of La incorporation at the lead titanate matrix through the tartrate precurser method.

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البروفسكيتى ودور نسبة اللانثانيوم $PbLa_xTi_{(1-3/4\times)}O_3$ دراسة التركيب البنائي وخواص العزل لسيراميك

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قسم الفيزياء- كلية الهندسة – جامعة مصر للعلوم والتكنولوجيا

في هذه الدراسة، تم تحضير سيراميك $PbLa_xTi_{(1-3/4\times)}O_3$ (PLT) باستخدام طريقة حمض الترتاريك بمحتوى La مختلف حيث (x = ٠.١،٠,٠٤،٠). تم عمل معالجه حرارية للعينات عند ٦٠٠ درجة مئوية وتم التأكد من تكوين المادة باستخدام حيود الأشعة السينية، والتحليل الطيفي للأشعة تحت الحمراء لتحويل فوريه، والمجهر الإلكتروني عالي الدقة وقياسات العزل الكهربي. أظهرت النتائج أن جميع العينات المطعمة بأيونات اللانثانيوم لها انتقال في التركيب البنائي من الدرجة الأولى من رباعي إلى مكعبي عند درجة حرارة كوري (Tc). ارتبط انتقال المرحلة هذا أيضًا بالانتقال من الطور الفرو كهربي إلى الطور شبه البارا كهربي. كشفت أطياف العزل الكهربائي أن المادة أظهرت سلوكًا كهربيًا مصحوب بعمليات الاسترخاء مع إزاحة Tc إلى قيم أعلى وزيادة ثابت العزل مع زيادة محتوى La حتى٠و٠,٠٤ = x . وتعزى الزيادة في ثابت العزل الكهربائي إلى انخفاض حجم الحبيبات في المدى تحت الدراسة من محتوي اللانثانيوم. علاوة على ذلك، أدت عملية التطعيم في تيتانات الرصاص (PT) إلى تكوين فراغات في الموقع A، مما أثر على درجة حرارة كوري. تسلط هذه الدراسة الضوء على إمكانية استخدام La أيونات كشائب في سيراميك PT لتحسين خصائصها الكهربية والضوئية، وتحديداً عن طريق تحفيز سلوك الاسترخاء.