Structural and Transport Properties of Calcium and lanthanum modified $PbTiO_3$

[1]Shweta Gupta, [2]Rajesh Kumar Katare
[1,2]Department of Physics, SAGE University, Indore,Madhya Pradesh,India.
Correspondence Email id-shweta90.gupta@gmail.com

Abstract

A solid-state ceramic method successfully created lead titanate ($PbTiO_3$; PT) particles. The amount of 90'domain reorientation in Calcium modified lead titanate piezoceramics, both with and without an applied field, was measured using an X-ray diffraction apparatus. Also determined is the spatial pole density distribution, which has the form [0 0 1]. In this study, we provide experimental results from our investigations into the role that parameters like calcium content, electric poling field, & microstructure play in determining the piezoelectric and electromechanical capabilities of ceramics. Particles of lead titanate ($PbTiO_3$) were synthesized using a solid-state ceramic technique. We calcined calcium granules from 500 to 1000 degrees Celsius at a rate of 5 degrees Celsius per minute for two hours. Transmission electron microscopy and X-ray diffraction analysis confirmed the formation of well-crystalline pure phase $PbTiO_3$ nanopowders after 900°C calcinations of the $PbTiO_3$. PbO and TiO_2 secondary phases were found when the powders were calcined at temperatures below 900 °C. Morphology and structure were evaluated using scanning electron microscopy (SEM). PLCT film shape and electric properties were investigated as a TiOx seed layer thickness. Both underwent a 600°C calcination to produce a single perovskite phase.

Keywords: *Lead titanate, Piezeoceramics, Perovskite structure, Solid-state ceramic*

DOI Number: 10.14704/nq.2022.20.13.NQ88079 **Neuro Quantology 2022; 20(13):595-600**

1. Introduction

Ceramics have long been valued for the unusual combination of mechanical strength, thermal resistance, electrical conductivity, optical transparency, and magnetic force. Ceramics are significant in various critical technologies, including communication, energy conservation and storage, electronics, and automation. Electro ceramics are sophisticated structural ceramic materials that are employed in electronics. The solid-state reaction approach was used to create single-phase polycrystalline samples of lead titanate with a perovskite structure. The processing settings have been tuned to produce phase pure, dense, crack-free, and homogenous models. SEM experiments have also examined the effect of sintering temperature and time on sample microstructure. The fracture surfaces of the sample sintered at 900°C are not visible in SEM micrographs, and the piece has produced a very homogeneous microstructure. The c/a ratio is roughly 1.04 and does not fluctuate appreciably with sintering temperature. Using a standard ceramic process, $PbTiO_3$ powder may be manufactured directly from the component oxide[1]. The development of these smart materials has matched the advancement of new technology. Piezoelectric materials are used in various sensors, actuators, transducers, and sonar; ferroelectrics have a high dielectric constant and are used in non-volatile memory; ferrites are used to store data and information; solid electrolytes are used to store and save energy; and so on.

Since certain perovskite crystals ($PbTiO_3$, $BaTiO_3$, $SrTiO_3$) exhibit ferroelectric properties and structural phase transitions, they have been of constant interest.$CaTiO_3$ is an alkaline earth metal titanate composed of earth-abundant nontoxic elements. $CaTiO_3$ exhibits excellent qualities as a multifunctional material, including optical properties, high dielectric constant, ferroelectricity, chemical stability, slight dielectric loss, low cost, and environmental friendliness. Several properties of $CaTiO_3$ have been explored owing to its broad applications.

$CaTiO_3$ shows electrical properties when applied to electronic devices such as capacitors and thermistors[11].

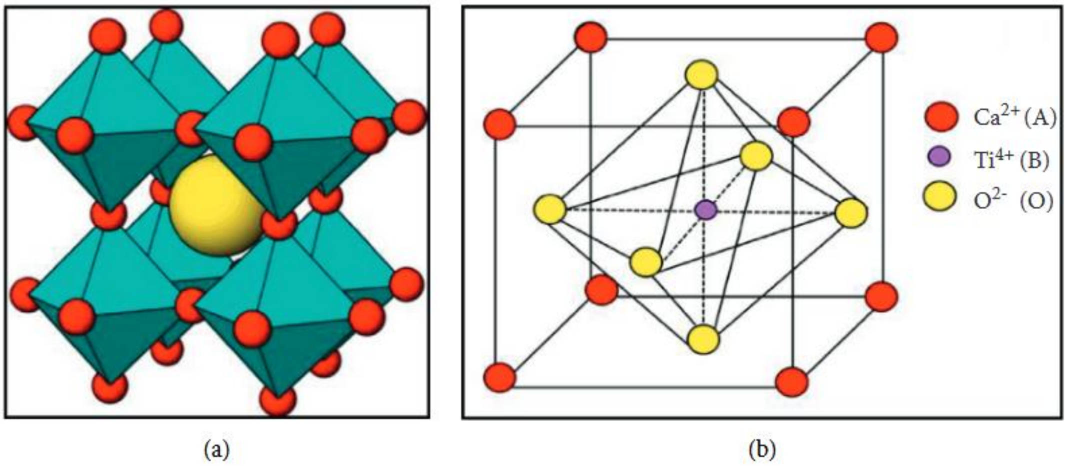

Fig.1*(a) Ideal cubic perovskite structure for ABO_3 (cyan, BO_6 units; yellow, A atoms) (Reprinted with permission from reference copyright from Elsevier). (b) Illustration of the crystal structure of $CaTiO_3$.*

Among these compounds, $PbTiO_3$ is considered to be among the most notable. It has high spontaneous polarization, low dielectric constant, high pyroelectric coefficient, and high Curie temperature. Although lead titanate ($PbTiO_3$, PT) is not a technologically relevant material on its own, it is a crucial component in many electronic devices, including capacitors, ultrasonic transducers, thermistors, & optoelectronics [2]. The combination of a high pyroelectric coefficient and a low permittivity makes this a good material for pyroelectric infrared detectors. $PbTiO_3$ (PT) is also widely employed in various piezoelectric applications. Lead titanate ($PbTiO_3$) is a perovskite ferroelectric material that exhibits a phase transition from tetragonal to cubic paraelectricity at a high Curie temperature Tc = 763 K. The reaction in the solid state ceramic technique occurs by diffusion between the powder particles in the solid state.

Lanthanum (La) – modified lead titanate or lead lanthanum titanate (PLT) is an important ferroelectric material characterized by its excellent dielectric, ferroelectric, pyroelectric, and electro-optic properties. The resulting PLT's permittivity increases with Tc when doping $PbTiO_3$ nanopowders with La, while its tetragonality decreases with increasing La content. In lanthanum that contains lead titanate, La^{3+} ions occupy Pb^{2+} sites and produce vacancies (□) in the cation lattice of ($Pb_{1-1.5x} La_x$ ‘□ $_{0.5x}$) TiO_3 ceramics. The transition temperature Tc decreases linearly with an increasing La^{3+} content[12].

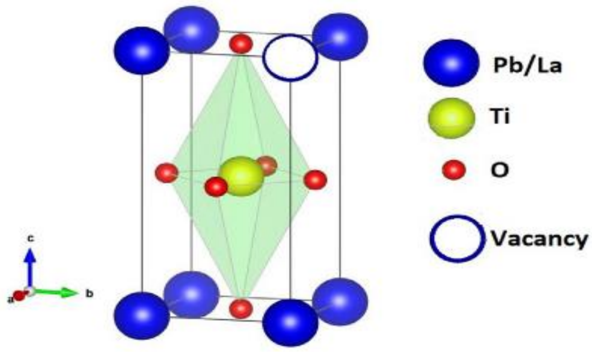

Fig.2*Atomic structure PLT unit cell perovskites and the positions of the ions in a tetragonal structure.*

The diffusing atoms are not equally dispersed, resulting in a non-homogeneous ceramic powder[8]. Chemical approaches can provide very excellent atomic-scale mixing. A pellet-shaped specimen is created utilizing a die and press setup. Here, the powder is mixed with a small amount of water or a binder like polyvinyl alcohol, then crushed in a die to form the desired shape[3]. A solvent-wet ceramic powder is destroyed in a container with an aperture, allowing a rod-like component to emerge. The resulting pellet is known as a "green pellet." These samples are burned at high temperatures in an appropriate environment to produce mechanical strength and microstructure. The development of single-phase cubic structured and non-uniform spherical particles was verified by XRD, SEM, and morphological analysis[9].

1.1 Structure of $PbTiO_3$: Pb and Ti are responsible for the ferroelectric properties of tetragonal $PbTiO_3$ because they occupy both 1a (0, 0, z) & 1b (1/2, 1/2, z) are Wyckoff positions. Three O atoms are visible, with two of them assigned to the O_1 orbital for 2c (1/2, 0) and one to the O_2 orbital for 1b (1/2, 1/2, z). More significant ionic deformations in the [0 0 1] direction are seen in the tetragonal structure than in the cubic paraelectric phase.

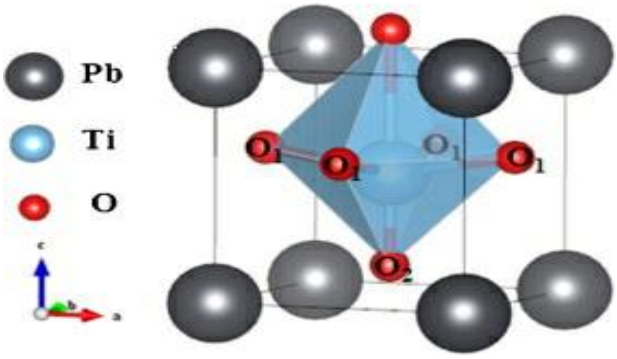

Fig.3*Structure of $PbTiO_3$*

In comparison to $BaTiO_3$-BT (120 °C) and Pb(Zr, Ti)O_3-PZT (360 °C), the dielectric constant of lead titanate $PbTiO_3$-PT is lower by orders of magnitude, and its Curie temperature is higher (490 °C). Because of its high spontaneous polarisation when cooled below the Curie temperature, bulk polycrystalline PT is difficult to manufacture by traditional sintering (T_C). At T_C, a tetragonal phase is formed with a tetragonality ratio of c/a = 1.064, resulting from a significant anisotropic thermal expansion (an increase in unit cell parameters along the tetragonal c axis and a decrease in the axis). Because of the high tetragonality ratio, the samples fracture and shatter the ceramic body[4].

Samples of lead titanate perovskite, a polycrystalline solid, were synthesized in a single phase using solid-state reaction synthesis. The processing settings have been tweaked to produce pieces that are phase pure, dense, crack-free, and consistent in appearance. X-ray diffraction patterns were analyzed to determine how PT-powders behaved throughout the sintering process. X-ray powder diffraction data was studied to validate phase formation and purity, as well as to learn about the characteristics and volume of the unit cell. The porosity of the samples was evaluated using X-ray density and bulk density. Using Scherrer's formula[6] the average particle sizes of pure phase models were determined from the X-ray peak width, and the influence of sintering temperature and time on sample microstructure was examined using SEM[7].

2. Experimental Procedures

2.1 Synthesis of pure Lead Titanate [$PbTiO_3$] and Calcium modified Lead Titanate (PCT)

The initial components were commercially available 99% pure Lead Carbonate, $PbCO_3$ (GR), and Titanium dioxide, TiO_3 (GR). The solid-state reaction of completely ground mixes of $PbCO_3$ and TiO_3 particles processed in an agate mortar in the requisite stoichiometric ratio will produce $PbTiO_3$ powder. The milling process takes 5 hours to complete. The powder sample is then calcined at 900°C for 5 hours.

$$PbCO_3 + TiO_2 \rightarrow PbTiO_3 + CO_2$$

The given equation is the reaction for the creation of $PbTiO_3$. Stoichiometric quantities of high-quality Calcium oxide, CaO, will be precisely weighed, and some manufactured Lead Titanate ($PbTiO_3$) powder will be added. This powder combination will be blended for 2 hours in an agate mortar. Purification is necessary for final product uniformity and removal of contaminants, and samples will be sintered in a silica crucible at 750oC for 5 hours. The sintered material will be cooled, crushed, and thoroughly processed again with the addition of an organic binder. This sintered material was then squeezed for 5 minutes using a hydraulic press at a pressure of 70 kg/m2. This well-dried powder will be formed into pellets of varying diameters. These pellets will be placed in a silica crucible and gradually heated to 850oC. They hold the temperature for 4 hours to finish the solid state sintering process[10]. To fulfill the criteria for electrical measurement, the spent sintered pellets will be cooled and polished, and silver paste will be applied.

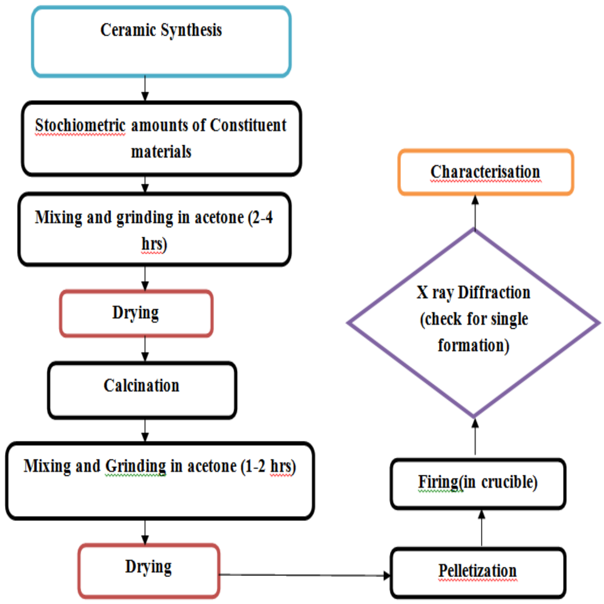

Fig.4*Block diagram of Ceramic Synthesis Procedure*

The solid-state ceramic technique produces a dielectric ceramic by grinding and heating a solid-state mixture of starting components. To improve reactivity, the starting ingredients (e.g., $PbCO_3$, TiO_2) for making $PbTiO_3$ are first weighed in suitable proportions and crushed into a fine powder. A mortar and pestle may create a tiny quantity of the mixture. However, utilizing ball-mills results in better mixing. A ball mill is a machine that contains little agate or steel balls of varying sizes in closed containers made of agate or steel. The mixture is coarsely crushed between the balls and the walls when the container rotates quickly back and forth. The ball mill may be operated continuously for many hours. The resulting powder is heated to high temperatures (calcined) to allow a solid-state reaction. X-ray diffraction examinations are used to verify the final product's production. The presence of peaks matching the starting components in the end product X-ray patterns suggests that the reaction is incomplete. Grinding and calcination are then repeated. The ceramic obtained in this manner is in powder form.

3. Results And Discussion

3.1 X-Ray Diffraction

Figure 5 shows the powder XRD patterns produced for powders calcined at 500°C, 600°C, 700°C, 800°C, 900°C, and 1000°C using an XRD (EMMA) GBC diffractometer in the range of Bragg's angle (2) 20°- 60°. The picture clearly shows that in the case of the sample calcined at 500 °C, crystallization begins to produce the perovskite PT phase with minor impurities of PbO and TiO_2. The XRD patterns for the pieces calcined at 600°C and 700°C reveal that the perovskite phase coexists with the PbO phase. However, it has been shown that the impurity phase steadily decreases from 700°C to that calcined at 800°C. PbO still exists in the sample calcined at 900°C, and the peaks of the perovskite phase are visible, demonstrating the creation of PT. As a result, the PbO phase steadily diminishes with increasing calcination temperature starting at 500 °C and vanishes at 1000 °C. A substantial intensity peak (2 = 31.85°) shows the creation of the perovskite PT phase, which corresponds to the JCPDS file no (060452). At 1000 °C, the XRD pattern indicates no undesirable step development such as TiO_2 or PbO, suggesting that the sol-gel procedure utilized in this work is a good approach for synthesizing $PbTiO_3$ Nanoparticles. The significant XRD peaks clearly show the existence of nanocrystallite particles. The crystallite size was determined from the XRD patterns using Scherer's formula (t = 0.9/cos) (where wavelength was utilized, - Full Width at Half Maximum (FWHM), and - diffraction angle).

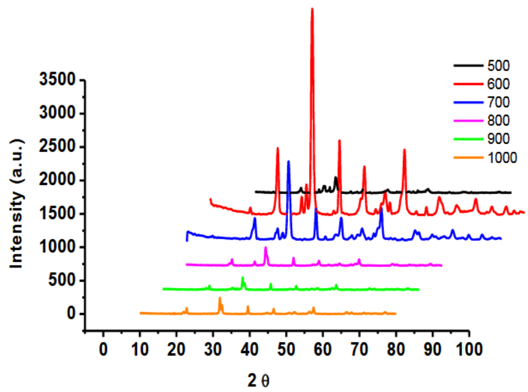

Fig.5*Pattern of X-ray diffraction of $PbTiO_3$ ceramics heated from 500°C to 1000°C.*

3.2 Optical Properties

UV-Visible Spectrophotometer (UV-300II, TECH COMP) was used to investigate the optical characteristics of the nanoparticles. The room temperature UV-Vis Transmission spectra electrochemically produced in the 700 to 1100 nm wavelength region are shown in Figure 5. The visual gap Eg is determined using the well-known Tauc plot using the following equation:

$$h\nu\alpha = (h\nu - E_g^{opt})^2$$

Where h represents the Plank constant, v represents frequency and is the optical band gap. The band gap energy was estimated for the sample at 1000 °C. As demonstrated in Figure 6, it produces 2.6 eV.

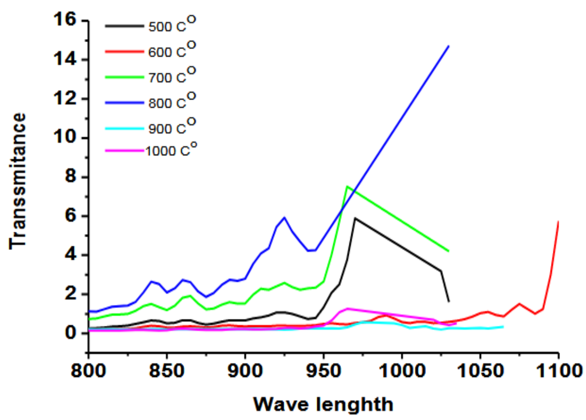

Fig.6*PT powder transmittance spectra after two hours of calcination at 500°C to 1000°C.*

3.3 Scanning Electron Microscope

In Figure 7, we see a scanning electron micrograph (SEM) showing the broken surface of $PbTiO_3$ samples that had been calcined at 1000°C and sintered at 1100°C for 2 hours (SEM: JOEL JSM-5500 LV scanning microscope JEOL). $PbTiO_3$ domains have a distinct form with a 180° domain wall.

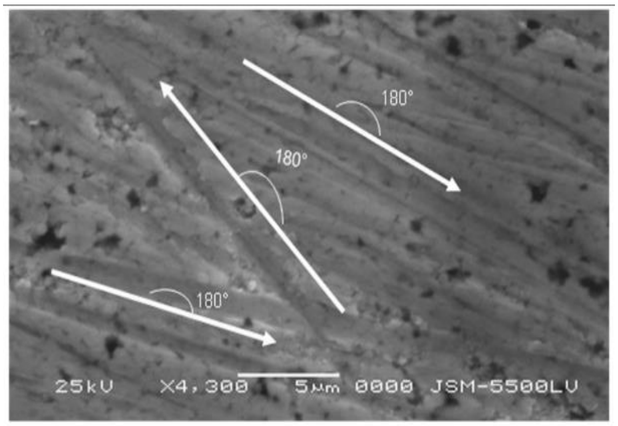

Fig.7*SEM photographs of the sample $PbTiO_3$ sintered.*

3.4 Fourier-Transform Infrared Spectroscopy Analysis

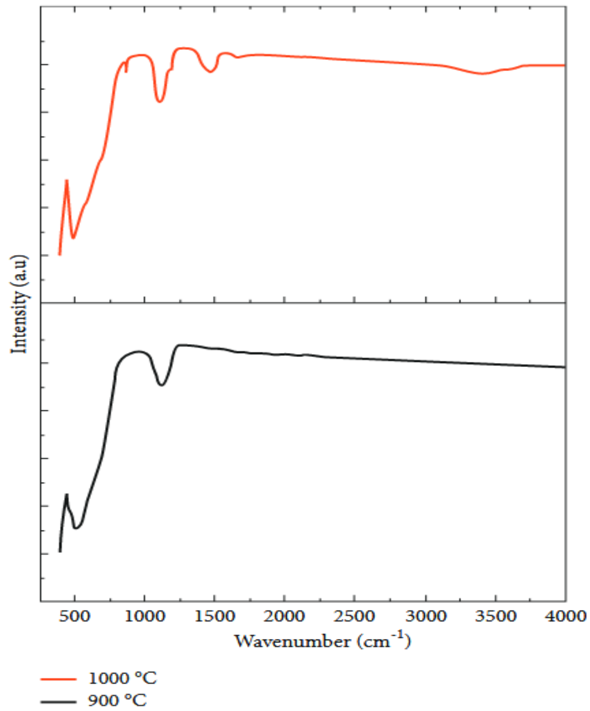

Fig.8*FTIR spectra of CaTiO3 obtained after calcination at 900°C and 1000°C.*

$PbTiO_3$ particles calcined at 900°C and 1000°C were analyzed using Fourier-transform infrared spectroscopy (FTIR). Figure 8 depicts the findings. The hallmark peak of the $PbTiO_3$ bond is given to the band at 570 cm^{-1}. The 460 cm^{-1} absorption peak may be traced back to the Ti-O-Ti bond's bending mode. Ti-O stretching vibration is defined by the absorption peak at 567 cm1. It indicates the presence of octahedral TiO_6 and the creation of a $CaTiO_3$ perovskite structure. The wide bands seen at 3644 cm1 and 3429 cm1 in $CaTiO_3$ powder produced at 1000°C are due to the superposition of the hydroxyl group's vibration band and the stretching vibration of the adsorbed OH group.

Conclusion

$PbTiO_3$ nanoparticles made by the Solid state ceramic method have studied their structure, optical, and dielectric properties. Based on the results of these tests, it can be concluded that $PbTiO_3$ nanoparticles were effectively generated during 2-hour calcinations at 1000 °C. Using SEM, we could demonstrate the existence of wall domains at 180°. A 2.6 eV energy discrepancy was observed. The Curie temperature, previously set at 635 degrees Celsius, suddenly dropped dramatically. SEM micrographs reveal that a sintered sample at 900 degrees Celsius has a relatively homogenous microstructure without any evidence of fracture surfaces. $PbTiO_3$ powder may be fabricated straight from the oxide components using standard ceramic synthesis techniques. Adding lanthanum raises the relative density to 98.5 percent and reduces the lattice isotropy to 1.023. Results from a dilatometric analysis indicate that the green sample shrank by 18% during the course of the whole sintering schedule, with soaking accounting for the majority of this size reduction.

References

[1]. V. A. Chaudhari and G. K. Bichile, "Synthesis, Structural, and Electrical Properties of Pure $PbTiO_3$ Ferroelectric Ceramics," *Smart Materials Research*, vol. 2013, pp. 1–9, May 2013, doi: 10.1155/2013/147524.

[2]. X. Lin, "Synthesis and Applications of Lithium-Doped Lanthanum Titanate Nanomaterials," p. 153.

[3]. S. K. Parida, R. N. P. Choudhary, and P. G. R. Achary, "Structure and ferroelectric properties of lead nickel tungsten titanate: $Pb(Ni_{1/3}Ti_{1/3}W_{1/3})O_3$ single perovskite," *Ferroelectrics*, vol. 551, no. 1, pp. 109–121, Oct. 2019, doi: 10.1080/00150193.2019.1658036.

[4]. S. Singh, O. P. Thakur, C. Prakash, and K. K. Raina, "STRUCTURAL AND DILATOMETRIC PROPERTIES OF LANTHANUM-SUBSTITUTED PCT CERAMICS," *Int. J. Mod. Phys. B*, vol. 20, no. 03, pp. 315–323, Jan. 2006, doi: 10.1142/S0217979206033280.

[5]. R. Abirami, T. S. Senthil, and C. R. Kalaiselvi, "Preparation of pure $PbTiO_3$ and (Ag–Fe) codoped $PbTiO_3$ perovskite nanoparticles and their enhanced photocatalytic activity," *Solid State Communications*, vol. 327, p. 114232, Mar. 2021, doi: 10.1016/j.ssc.2021.114232.

[6]. L. Pan and G. Zhu, Eds., *Perovskite Materials - Synthesis, Characterisation, Properties, and Applications*. InTech, 2016. doi: 10.5772/60469.

[7]. K. S. Shankar and A. K. Raychaudhuri, "Low-temperature polymer precursor-based synthesis of nanocrystalline particles of lanthanum calcium manganese oxide ($La_{0.67}Ca_{0.33}MnO_3$) with enhanced ferromagnetic transition temperature," *J. Mater. Res.*, vol. 21, no. 1, pp. 27–33, Jan. 2006, doi: 10.1557/jmr.2006.0031.

[8]. J. Wang *et al.*, "Influence of the dynamic lattice strain on the transport behavior of oxide heterojunctions," *Appl. Phys. Lett.*, vol. 102, no. 2, p. 022423, Jan. 2013, doi: 10.1063/1.4788731.

[9]. S. Fathima, S. Sharmila, and V. S. Kumar, "FACILE SYNTHESIS OF IRON DOPED LANTHANUM NICKEL OXIDE," p. 9.

[10]. M. K. Gerges, M. Mostafa, and G. M. Rashwan, "Structural, optical and electrical properties of $PbTiO_3$ nanoparticles prepared by Sol-Gel method," p. 9.

[11]. M. Mostafa, Z. A. Alrowaili, G. M. Rashwan, and M. K. Gerges, "Ferroelectric behavior and spectroscopic properties of La-Modified lead titanate nanoparticles prepared by a sol-gel method," *Heliyon*, vol. 6, no. 2, p. e03389, Feb. 2020, doi: 10.1016/j.heliyon.2020.e03389.

[12]. M. Mostafa, Z. A. Alrowaili, M. M. Al Shehri, M. Mobarak, and A. M. Abbas, "Structural and Optical Properties of Calcium Titanate Prepared from Gypsum," *Journal of Nanotechnology*, vol. 2022, pp. 1–9, Mar. 2022, doi: 10.1155/2022/6020378.