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Synthesis and Structural Tuning of Rare-Earth Doped Lead Zirconate Titanate (PZT) Ceramics for Enhanced Ferroelectric Properties

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Abstract: *Lead Zirconate Titanate (PZT), being one of the most investigated ferroelectric ceramics, has attracted much attention because of its superior dielectric, piezoelectric, and electromechanical properties, especially around the Morphotropic Phase Boundary (MPB). In practical applications, however, long-term performance capabilities of doped PZT ceramics are generally limited because of their susceptibility to degradation caused by electrical fatigue, aging, evaporation of lead, or thermal instability.*

In this investigation, research on the structural and ferroelectric characteristics of rare earth-doped PZT ceramics was focused, specifically on lanthanum-doped PZT ceramics, substituted by 2 mol% lanthanum, doped on the composition located at/around the MPB. The PZT ceramics studied were prepared through sol-gel processing. Structural analyses were undertaken, and structural characterization was accomplished through X-ray diffraction (XRD) measurements. The diffraction data revealed that there was single-phase perovskite formation without secondary phases. The addition of lanthanum resulted in broader peaks and reduced intensity, reflecting lattice distortion and reduction in crystallites. The results prove that the doping of rare-earth elements is an effective method for carrying out controlled structural modifications of PZT ceramics for use in advanced ferroelectric devices.

Keywords: Lead zirconate titanate, rare-earth doping, lanthanum-doped PZT, morphotropic phase boundary, ferroelectric ceramics, X-ray diffraction.

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Introduction:

Ferroelectric materials are characterized by the existence of a spontaneous electric polarization, which can be reversed by the application of an external electric field. This is due to the absence of a center of symmetry in the crystal lattice composed of ions. Ferroelectric materials are multifunctional. Moulson A.J. and Herbert J.M. (2003) in their work have shown that Ferroelectric ceramics are important because they have several unique properties. These include high dielectric constants, piezoelectricity, pyroelectricity, as well as excellent electromechanical coupling. These materials are used in applications such as sensors, actuators, ultrasonic transducers, memory devices, and energy harvesters.

Lines M.E. and Glass A.M. (1977) in their work stated that of the different ferroelectric materials that have been generated, the perovskite oxides with the formula ABO_3 have gathered much attention. In these materials, ferroelectric properties are mainly originated from the shift of the cation situated on the B-position with respect to the octahedral oxygen. Lead Zirconate Titanate with the formula $Pb(Zr_xTi_{1-x})O_3$ or PZT is one of the highly adopted forms of the perovskite ferroelectric ceramics.

Jaffe B. *et al.* (1971) reported that one of the distinct characteristics observed in PZT is the occurrence of a morphotropic phase boundary (MPB) around Zr/Ti composition ratios of about 52/48. This is where phases involving the tetragonal and rhombohedral structures coexist. Haertling G.H. (1999) stated that this is because, at this composition, the difference in free energy between phases is very small. This resulted in the vicinity of the MPB in PZT having exceptionally large dielectric constants and piezoelectric coefficients.

Moulson A.J. and Herbert J.M. (2003) in their work mentioned that although PZT is of prime technological interest, there are certain inherent limitations in undoped PZT ceramics. High-temperature processing causes lead volatilization, thereby creating oxygen vacancies, leading to increased dielectric loss as well as leakage current. Additionally, Scott J.F. in his work showed that electric cycling causes fatigue effects, while defect migration causes aging of ferroelectric properties over prolonged periods of time. To overcome these drawbacks, compositional modulation through doping has been used effectively.

The strong possibility of precipitation, low solubility, or a combination of both, makes lanthanum, neodymium, samarium, and praseodymium prefer the Pb^{2+} ion-site in a perovskite lattice because of similarities in ionic size, acting as donor-type dopants. The rare earth elements decrease oxygen vacancies, leading to improved densification, domain wall mobility, and stabilization of crystal structures. In this design, this paper highlights the fabrication and structural characterization of un-doped, as well as 2 mol% doped lanthanum, PZT ceramic materials using a sol-gel processing technique.

Experimental Methodology:

Materials: All precursor chemicals used in this work were of analytical reagent grade. Lead acetate trihydrate, zirconium propoxide, titanium isopropoxide, and lanthanum nitrate hexahydrate served as the primary sources for Pb, Zr, Ti, and La, respectively. Appropriate care was taken in order to ensure the accuracy in stoichiometry while weighing and preparing solutions.

Table 1. Raw Material Calculation for 10 g Undoped PZT Sample

Composition: $Pb(Zr_{0.52}Ti_{0.48})O_3$

Raw Material	Molar Ratio	Molar Mass (g/mol)	Weight Fraction	Required Mass (g)
PbO	1.00	223.20	0.685	6.85
ZrO_2	0.52	123.22	0.197	1.97
TiO_2	0.48	79.87	0.118	1.18
Total	—	—	1.000	10.00

Table 2. Raw Material Calculation for 10g 2% La-Doped PZT Sample

Composition: $Pb_{0.98}La_{0.02}(Zr_{0.52}Ti_{0.48})O_3$

Raw Material	Molar Ratio	Molar Mass (g/mol)	Weight Fraction	Required Mass (g)
PbO	0.98	223.20	0.674	6.74
La_2O_3	0.01	325.81	0.010	0.10
ZrO_2	0.52	123.22	0.197	1.97
TiO_2	0.48	79.87	0.118	1.18
Total	—	—	1.000	10.00

Fig. 1. Step-by-step photographic representation of the Sol-gel synthesis of PZT/La-doped PZT

Sol–Gel Synthesis:

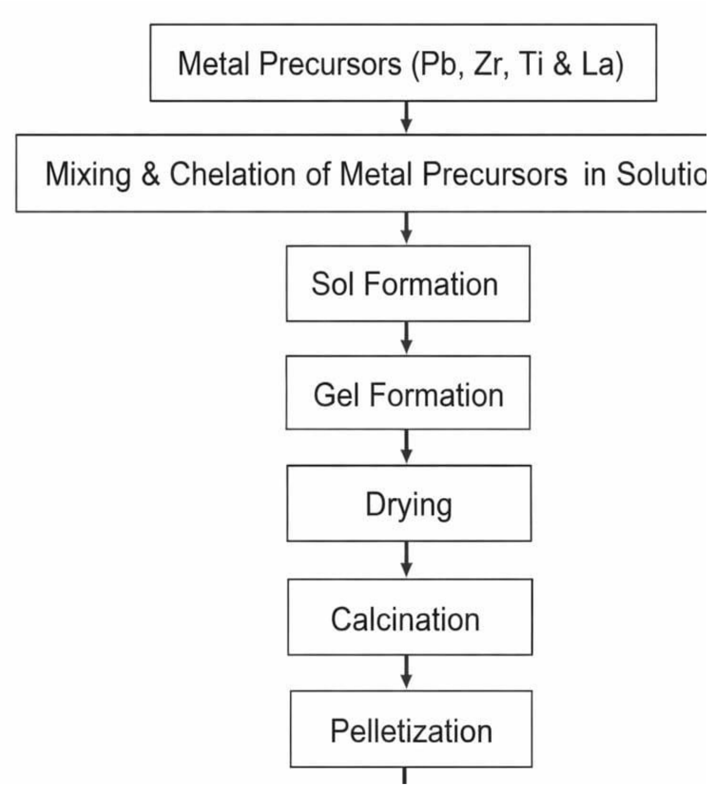

Fig. 2. Flowchart of the sol–gel synthesis process.

According to Brinker C.J. and Scherer G.W. (1990) the Sol-gel method has been adopted to attain homogeneous ion mixture at the molecular scale and to lower the calcination temperature. Appropriate quantities of the lead precursor and Zr-Ti alkoxides equivalent to the MPB formulas $Pb(Zr_{0.52}Ti_{0.48})O_3$ were separately dissolved in reactive solvents. For the doped formula, 2% La was incorporated at the lead substitution. Hydrolysis and condensation reactions led to the development of a sol that eventually evolved to the gel state. After the sol-gel process, the dried xerogel was calcined at 700°C to 750°C to yield the crystalline powders of the ferroelectric material PZT.

Structural Characterization: Powder samples were ground into fine powders to reduce preferred orientation effects prior to X-ray diffraction analysis, according to the procedure reported by Cullity and Stock (2001); XRD measurements were performed by using Cu–Kα radiation (λ = 1.5406 Å) at a scan interval from 20° to 80° in 2θ. The phase identification was done by match comparison with standard JCPDS data, while the average crystallite size was determined by using the Scherrer equation.

Results and Discussion

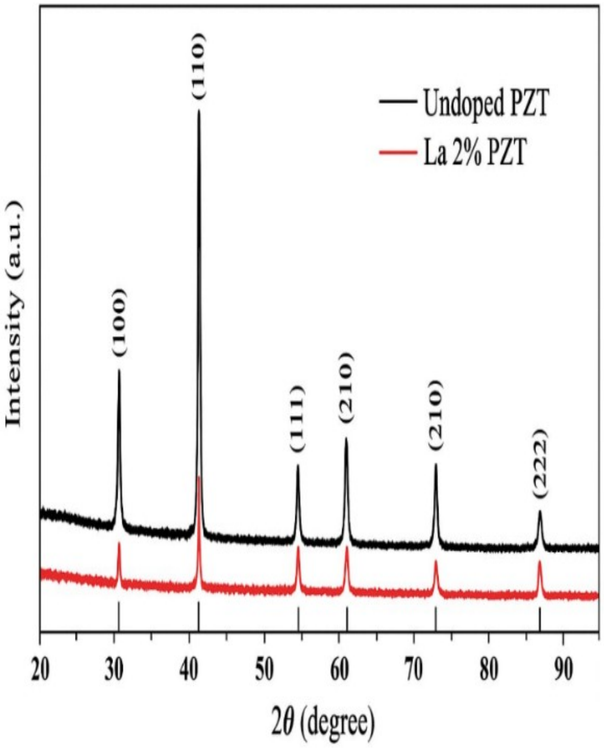

Fig. 3. X-ray diffraction patterns of undoped PZT and 2% La-doped PZT.

X-Ray Diffraction Analysis:

Table 3. Final calculated structural parameters (d-spacing, lattice constants, and crystallite size) of undoped and 2% La-doped PZT obtained from XRD analysis

Sample	2θ (110)	d (Å)	Lattice constant a (Å)	Crystallite size (nm)
Undoped PZT	40°	2.25	3.18	~42 nm
2% La-PZT	40°	2.25	3.18	~28 nm

According to Jaffe B. *et al.* (1971), compositions near the morphotropic phase boundary show a tetragonal phase, as evidenced by the separation of the (200)/(002) reflections in the XRD pattern. The results of the XRD analysis show that the tetragonal PZT phases are formed. In this respect, it has been discussed by Moulson A.J. and Herbert J.M. (2003) that the degree of dopant substitution tends to introduce lattice strain and restrict grain growth. Hence, it is evident that the reduction in crystallite size from ~42 nm for undoped PZT to ~28 nm for 2% La-doped PZT is attributed to lattice distortion and grain refinement effects.

The figure 3 shows XRD patterns of undoped and 2 mol % La-doped PZT ceramics: both the undoped and La-doped compositions display sharp diffraction peaks that are characteristic of the perovskite phase, confirming the formation of a single perovskite phase. No additional peaks related to secondary phases, such as pyrochlore, are observed, indicating that the lanthanum ions have effectively substituted into the PZT lattice.

These strong reflections at 31°, 38°, 45°, 56°, and 66° are characteristic of the perovskite PZT structure and are consistent with diffraction patterns given by Jaffe B. et al.(1971). From the figure, it can also be seen that the similarity in the diffraction patterns of both compositions is quite close, indicating that lanthanum substitution has not significantly changed the crystal symmetry of PZT, as given by Moulson et. al. (2003).

Effects of Lanthanum Substitution: According to Jaffe B. *et al.* (1971) in comparison to the undoped sample, lanthanum-doped PZT shows broader peaks along with reduced intensity. This phenomenon could be attributed to lattice distortion, as well as reduced crystallite size because of ion substitution at the A-site due to the higher concentration of La^{3+} ions over Pb^{2+} ions. This is because of the smaller size of the La^{3+} ion, which causes lattice strain.

D. Damjanovic's (1998) work shows that the reduction in crystallite size using the broadening of peaks is beneficial for ferroelectric properties, as it enhances the concentration of domain walls and aids in polarization rotation. In addition, Noheda B. (1999) work shows the coexistence of both tetragonal and rhombohedral phases around the (200)/(002) reflection region implies the stabilization of the morphotropic phase boundary, which is proven to improve the dielectric and piezoelectric properties.

In general, according to Brinker C.J. and Scherer G.W. (1990) the results from the XRD studies have shown that the addition of 2 mol% of lanthanum in PZT has resulted in the successful modulation of the crystal structure of PZT.

Conclusion:

Routine samples of undoped PZT ceramic materials and 2-mol% lanthanum doped PZT ceramic samples were prepared through the sol–gel method. Further structural characterization analysis through the X-ray diffraction method unveiled the single-phase characteristics of the synthesized ceramic materials. As discussed by Moulson et. al. (2003) the addition of lanthanum to the PZT ceramic allows for controlled lattice distortions without the loss of the overall symmetry within the crystalline structure.

The role of structural transformations brought about by lanthanum doping with regard to morphotropic phase boundary stabilization and domain wall mobility is squarely intertwined with creativity for ferroelectric performance. The current research clearly supports that doping with rare earths is a valid and practical approach suitable for creating PZT ceramics with a robust structure for ferroelectric applications.

Future Scope:

1. Examination of a wider concentration of lanthanum to optimize the doping levels for better ferroelectric properties.
2. Detailed electrical property measurements, such as dielectric, ferroelectric (P-E loop), and piezo, to determine structure property relationships.
3. Temperature-dependent XRD measurements for examining phase stability around the Curie temperature.
4. Fabrication and Characterization of Lanthanum-Doped PZT Thin Films with Applications in Microelectromechanical Systems.
5. Long-term reliability testing such as fatigue, aging, and thermal cycling testing.

References:

Brinker, C.J. and Scherer, G.W. (1990). Sol–Gel Science: The Physics and Chemistry of Sol–Gel Processing. San Diego: Academic Press.

Cullity, B.D. and Stock, S.R. (2001). Elements of X-Ray Diffraction, 3rd ed. Upper Saddle River: Prentice Hall.

Damjanovic, D. (1998). “Ferroelectric, dielectric and piezoelectric properties of ferroelectric thin films and ceramics,” Reports on Progress in Physics, vol. 61, no. 9, pp. 1267–1324.

Haertling, G.H. (1999). “Ferroelectric ceramics: History and technology,” Journal of the American Ceramic Society, vol. 82, no. 4, pp. 797–818.

Jaffe, B., Cook, W.R. Jr. and Jaffe, H. (1971). Piezoelectric Ceramics. London: Academic Press.

Lines, M.E. and Glass, A.M. (1977). Principles and Applications of Ferroelectrics and Related Materials. Oxford: Clarendon Press.

Moulson, A.J. and Herbert, J.M. (2003). Electroceramics: Materials, Properties, Applications, 2nd ed. Chichester: Wiley.

Noheda, B., Cox, D.E., Shirane, G., Gonzalo, J.A., Cross, L.E. and Park, S.E. (1999). “A monoclinic ferroelectric phase in the $Pb(Zr_{1-x}Ti_x)O_3$ solid solution,” Applied Physics Letters, vol. 74, no. 14, pp. 2059–2061.

Scott, J.F. (2000). Ferroelectric Memories. Berlin: Springer.