Rare Earth Ion (La$^{3+}$) Doped BaTiO$_3$ Perovskite Nanoceramics for Spintronic Applications

B. H. Devmunde$^1$, Saurabh B. Somwanshi$^2$, Prashant B. Kharat$^3$, Madhukar B. Solunke$^4$

Department of Physics, Vivekanand Arts, Sardar Dalip Singh Commerce and Science College, Aurangabad – 431005, Maharashtra, India

Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad – 431004, Maharashtra, India

Department of Physics, Vinayak Vidhyalaya Mahavidyalaya, Nandgaon Khandeshwar, Amravati – 444708, Maharashtra, India

Department of Physics, Vasantrao Naik College, Aurangabad – 431003, Maharashtra, India

Corresponding author e-mail : bhdevmunde05@gmail.com

Abstract. The present study reports the structural and morphological investigation of La$^{3+}$ doped BaTiO$_3$ nanoceramics prepared by combustion synthesis. The effect of La$^{3+}$ doping on the structural and morphological properties was examined by the X-Ray diffraction (XRD), transmission electron microscopy (TEM) and selected area electron diffraction (SAED) technique. Room temperature XRD analysis shows that prepared samples are in a single phase with the tetragonal structure. Structural parameters like average crystallite size ($D$) and lattice constant ($a$ and $c$) were calculated from the XRD data. The surface morphology of the samples was studied by transmission electron microscopy (TEM) technique. It was found that the nanoparticles are in tetragonal shape with agglomeration to some extent. All the outcomes show that La doped BaTiO$_3$ nanoceramics are promising candidates for spintronic applications.

1. Introduction
Recently, ABO$_3$ structured perovskite materials are broadly utilized for logical and mechanical applications. It tends to be material for configuration of modern electronic gadgets because of its momentous electronic properties. The perovskite materials are notable for a few noteworthy properties like ferroelectric, piezoelectric, magnetocaloric and optical, dielectric and ferromagnetic properties and so forth [1-5]. A portion of the perovskite material shows multiple properties are those known as multiferroic materials. These days, multiferroic is a current and a hotly debated issue for the hardware business because of its critical property and applications. Essentially, properties of the material are relied upon the structure, synthesis and other a few factor like a combination strategy, synthesis condition and other parameters [6]. For the most part, perovskite ceramics are set up by solid state reactions which require high temperature or additional time span. Combination of perovskite through wet chemical techniques was conveyed at moderate temperature for the one of kind physical,
electrical, optical, electronic and magnetic properties [7]. Sol-gel auto ignition has as of late become a well known procedure because of straightforward cycle, low sintering temperature, time and energy utilization than other customary strategies [8-9]. Hence, the sol-gel strategy is utilized to improve properties with greater homogeneity and constrained molecule dispersion this will have an effect on basic, electrical and optical properties of perovskite.

Nano-sized perovskite structured BaTiO$_3$ ceramics have pulled in the significant consideration of researchers and technologists because of its multi-usefulness. These ordinary perovskite materials have high dielectric constant, low dielectric loss, and superior thermal stability. Subsequently, the specialist put forth attempts to improve their properties which will be valuable for the different advancements. It has been seen that materials which have a high dielectric constant additionally have high dielectric loss and high dielectric constant with a high loss in a material can cause significant impedance mismatch issues. So to defeat these issues it is important to bring down both dielectric constant and dielectric loss, which can be accomplished somewhat by replacing Ba site in BaTiO$_3$ by rare earth ions such as La$^{3+}$, Gd$^{3+}$, Dy$^{3+}$, Nd$^{3+}$ etc. It has application in unique dynamic random access memory, ceramic capacitors, in the sensor as pyroelectric sensors, chemical sensors, biosensors, microwave gadgets, infrared detectors and optoelectronic applications [10-16]. Considering the above points, the aim of the current work was to incorporate La$^{3+}$ doped barium titanate nanoceramics utilizing sol-gel auto burning technique and to investigate the role of La$^{3+}$ doping on the structural and morphological properties.

2. Experimental

Analytical (AR) grade barium nitrate hexahydrate (Ba(NO$_3$)$_2$·6H$_2$O), Lanthanum nitrate hexahydrate ((La(NO$_3$)$_3$·6H$_2$O), tetra butyl titanate (Ti(OC$_4$H$_9$)$_4$), citric acid (C$_6$H$_5$O$_7$), ethanol (C$_2$H$_5$-OH) and ammonium hydroxide (NH$_4$OH) provided by Merck with ~99 % purity were used as a precursor materials without further purification. The pure and La$^{3+}$ doped BaTiO$_3$ nanoceramics with general formula Ba$_{1-x}$La$_x$TiO$_3$ (where x = 0.00 and 0.002) were synthesized using sol-gel auto combustion technique. Firstly, tetra butyl titanate solution diluted with ethanol was added into the citric acid aqueous solution with pH = 8 which is adjusted by adding the appropriate amount of ammonia solution. Ethanol was used to chelate tetra butyl titanate (molar ratio of 1:2) to obtain a highly condensed product and to promote the gelification process. After being stirred at 80 °C for 1 h, a yellowish transparent liquid was obtained. At the same time, barium nitrate and lanthanum nitrate were dissolved separately into distilled water. Subsequently, both the solutions were poured together. At the same time, the pH value was adjusted to be 7 using ammonia until a transparent liquid was achieved. Followed by a continuous stirring for 3 h, the viscosity of the solution increased gradually and then a stable transparent sol formed. Continuous heating of 110 °C initiates the gel formation. Under constant stirring and heating, viscous gel transforms into a dry gel. The combustion process of nitrate–citrate gel was formed and the obtained powders dried, crushed and were sintered at 950°C for 4 h in a muffle furnace in order to get the nanocrystalline powders. The crystalline phase of the samples was examined by X-Ray Diffraction System Ultima IV of Rigaku Corporation, Japan at room temperature. The pattern was recorded by Cu-Kα radiation ($\lambda$=1.5418Å) in the 20 range of 20–80° with a step size 0.01° and time/step 2s was used. The microstructural studies were investigated through transmission electron microscopy (TEM) technique and selected area electron diffraction (SAED) technique.

3. Results and discussion

The X-ray diffraction (XRD) patterns of Ba$_{1-x}$La$_x$TiO$_3$ (where x = 0.00 and 0.002) are shown in Fig. 1 (a). All the indexed peaks show the tetragonal phase of the La doped BaTiO$_3$ sample [17-19]. The XRD patterns revealed that the prepared powder was single phase crystalline in nature with (110) peak (Fig. 1 (b)) as the dominant peak without any impurity. All the Bragg reflections present in Fe doped powder X-ray diffraction pattern (100), (110), (111), (200), (201) (211), (220), (212) and (310) could be indexed as main tetragonal perovskite reflections and confirmed the phase purity (JCPDS No. 89-
The average crystallite size was calculated using Debye Scherrer’s formula. The other structural parameters like lattice constant \((a, c)\), \(c/a\) ratio, unit cell volume \((V)\), X-ray density \((d_X)\), bulk density \((d_B)\), and crystallite size \((t)\) were calculated from XRD analysis and their formulae are reported in our previous research report [20-24]. The values of different structural parameters are given in table 1. It is noted from Table 1 that all the structural parameters were decreases after La doping.

![XRD pattern](image1.png)

**Fig. 1** XRD pattern and (110) peak of \(Ba_{1-x}La_xTiO_3\) (where \(x = 0.00\) and \(0.002\))

| Sample        | \(a\) (Å) | \(c\) (Å) | \(c/a\) | \(V\) (Å³) | \(d_X\) (g/cm³) | \(d_B\) (g/cm³) | \(t\) (nm) | \(D\) (nm) |
|---------------|-----------|-----------|---------|-----------|----------------|----------------|----------|-----------|
| \(BaTiO_3\)   | 3.990     | 4.042     | 1.013   | 64.35     | 6.017          | 5.563          | 16       | 17.62     |
| \(Ba_{0.98}La_{0.02}TiO_3\) | 3.988 | 4.016 | 1.007 | 63.87 | 5.802 | 5.472 | 18 | 19.28 |

The morphological studies of the \(Ba_{1-x}La_xTiO_3\) (where \(x = 0.00\) and \(0.002\)) nanoceramics were investigated by TEM. Fig. 2 shows TEM images with particle size distribution and SAED patterns of both the samples. Fig. 2 indicates that the shape of the nanoparticles is approximately tetragonal with an agglomeration to smaller extent. The average particles sizes \((D)\) from TEM analysis for the pure and La doped \(BaTiO_3\) nanoceramics was found to be 17.62 nm and 19.28 nm respectively which is in good agreement with the XRD calculations. The corresponding SAED pattern of the typical samples confirms that the nanoparticles possess the tetragonal structure having nanocrystalline nature. The SAED consists of concentric sharp rings, which well matches with the standard tetragonal structure of \(BaTiO_3\). The SAED patterns also shows the superimposition of the bright spots with a Debye ring pattern which indicates that the prepared samples are nanocrystalline in nature [25-26].
4. Conclusions

La$^{3+}$ doped BaTiO$_3$ nanoceramics were successfully prepared by solution combustion synthesis. The effect of La$^{3+}$ doping on the structural and morphological properties was examined by the XRD, TEM and SAED. Room temperature XRD analysis shows that prepared samples are in a single phase with the tetragonal structure. Structural parameters like average crystallite size ($D$) and lattice constant ($a$ and $c$) were calculated from the XRD data. All the structural parameters were decreased after La doping. It was found that the nanoparticles are in tetragonal shape with agglomeration to the some extent. The particle size calculated from TEM was decreased after La doping. All the outcomes show that La doped BaTiO$_3$ nanoceramics are promising candidates for spintronic applications.

References

[1] Shisode, M.V., et al., Investigations of magnetic and ferroelectric properties of multiferroic Sr-doped bismuth ferrite. Applied Physics A, 2018. 124(9): p. 603.

[2] Khirade, P. P., Birajdar, S. D., Raut, A. V., & Jadhav, K. M. (2016). Multiferroic iron doped BaTiO$_3$ nanoceramics synthesized by sol-gel auto combustion: influence of iron on physical properties. Ceramics International, 42(10), 12441-12451.

[3] Wang, Z., et al., Magnetocaloric effect in perovskite manganites La 0.7– x Nd x Ca 0.3 MnO 3 and La 0.7 Ca 0.3 MnO 3. Journal of Applied Physics, 2001. 90(11): p. 5689-5691.

[4] Kim, Y.-I., et al., Characterization of the structural, optical, and dielectric properties of oxynitride perovskites AMO$_2$N ($A=$ Ba, Sr; Ca; $M$= Ta, Nb). Chemistry of materials, 2004. 16(7): p. 1267-1276.

[5] Bhoyar, D.N., et al., Structural, infrared, magnetic and ferroelectric properties of Sr0·5Ba0·5Ti1-xFexO3 nanoceramics: Modifications via trivalent Fe ion doping. Physica B: Condensed Matter, 2020. 581: p. 411944.

[6] Ye, Z.-G., Handbook of advanced dielectric, piezoelectric and ferroelectric materials: Synthesis, properties and applications. 2008: Elsevier.

[7] Macwan, D., P.N. Dave, and S. Chaturvedi, A review on nano-TiO2 sol–gel type syntheses and its applications. Journal of materials science, 2011. 46(11): p. 3669-3686.

[8] Sutka, A. and G. Mezinskis, Sol-gel auto-combustion synthesis of spinel-type ferrite nanomaterials. Frontiers of Materials Science, 2012. 6(2): p. 128-141.

[9] Cole, M., et al., Low dielectric loss and enhanced tunability of Ba 0.6 Sr 0.4 TiO 3 based thin films via material compositional design and optimized film processing methods. Journal of applied physics, 2003. 93(11): p. 9218-9225.

[10] Kumar, A. and S.G. Manavalan, Characterization of barium strontium titanate thin films for tunable microwave and DRAM applications. Surface and Coatings Technology, 2005. 198(1-3): p. 406-413.

[11] Chilibon, I. and J.N. Marat-Mendes, Ferroelectric ceramics by sol–gel methods and applications: a review. Journal of sol-gel science and technology, 2012. 64(3): p. 571-611.

[12] Gorzkowski, E., et al., Glass-ceramics of barium strontium titanate for high energy density
capacitors. Journal of electroceramics, 2007. **18**(3-4): p. 269-276.

[13] Fang, X., et al., *Dielectric film for biosensor application*. Sensors and Actuators B: Chemical, 2006. **119**(1): p. 78-83.

[14] Buniatyan, V.V., et al., *pH-sensitive properties of barium strontium titanate (BST) thin films prepared by pulsed laser deposition technique*. physica status solidi (a), 2010. **207**(4): p. 824-830.

[15] Bao, P., et al., *Barium strontium titanate thin film varactors for room-temperature microwave device applications*. Journal of Physics D: Applied Physics, 2008. **41**(6): p. 063001.

[16] Liang, X., Z. Meng, and W. Wu, *Effect of acceptor and donor dopants on the dielectric and tunable properties of barium strontium titanate*. Journal of the American Ceramic Society, 2004. **87**(12): p. 2218-2222.

[17] Saeed, A., et al., *Structural and dielectric properties of iron doped barium strontium titanate for storage applications*. Journal of Materials Science: Materials in Electronics, 2015. **26**(12): p. 9859-9864.

[18] Guo, Z., et al., *Structural and multiferroic properties of Fe-doped Ba0. 5Sr0. 5TiO3 solids*. Journal of Magnetism and Magnetic Materials, 2013. **325**: p. 24-28.

[19] Kaur, A., et al., *Structural, magnetic and electronic properties of iron doped barium strontium titanate*. RSC Advances, 2016. **6**(113): p. 112363-112369.

[20] Bhoyar, D.N., et al., *Doping Effect of Fe Ions on the Structural, Electrical, and Magnetic Properties of SrTiO 3 Nanoceramic Matrix*. Journal of Superconductivity and Novel Magnetism, 2018: p. 1-12.

[21] Somvanshi, S.B., et al., *Structural, thermal, spectral, optical and surface analysis of rare earth metal ion (Gd3+) doped mixed Zn–Mg nano-spinel ferrites*. Ceramics International, 2020.

[22] Bhosale, A., et al., *Influential incorporation of RE metal ion (Dy3+) in yttrium iron garnet (YIG) nanoparticles: Magnetic, electrical and dielectric behaviour*. Ceramics International, 2020.

[23] Somvanshi, S.B., et al., *Hyperthermic evaluation of oleic acid coated nano-spinel magnesium ferrite: enhancement via hydrophobic-to-hydrophilic surface transformation*. Journal of Alloys and Compounds, 2020: p. 155422.

[24] Somvanshi, S.B., et al., *Influential diamagnetic magnesium (Mg2+) ion substitution in nano-spinel zinc ferrite (ZnFe2O4): thermal, structural, spectral, optical and physisorption analysis*. Ceramics International, 2020. **46**(7): p. 8640-8650.

[25] Wang, X.-H., et al., *The grain size effect on dielectric properties of BaTiO3 based ceramics*. Materials Science and Engineering: B, 2003. **99**(1-3): p. 199-202.

[26] Green, M.A., et al., *Optical properties of photovoltaic organic–inorganic lead halide perovskites*. The journal of physical chemistry letters, 2015. **6**(23): p. 4774-4785.