CHAPTER -5
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5.1 INTRODUCTION

The preparation of ceramics is a challenging task of highly interdisciplinary character. It involves physical chemistry, chemical engineering apart from physics and electronics. Among the most widely investigated ceramics are perovskite ferroelectrics with general formula ABO₃ (A = mono or divalent B = trivalent - hexavalent). Modified lead titanate is an important member of perovskite type ferroelectric family. Fabrication process parameters have a significant effect on all physical and electrical properties of ceramics and their applications. The key stages in the fabrication of ceramics are calcination and sintering which are sometimes combined. During these processes constituent atoms redistribute themselves in such a way as to minimize the free energy of the system involved. The most economical method for ceramic preparation is metal oxide (MO) process [1] and various steps involved in this process are given in flow diagram shown in fig. 5.1.

5.2 Preparation of composition

The material preparation is basically controlled by the composition but it is also affected by grain size and porosity of the sintered ceramic, and the latter features are affected by the method of fabrication. In fact, one of the very significant advantage of ceramic ferroelectrics is the case with which
Additional and substitution of alternative cations in ABO₃ type perovskites can (1) shift the Curie point, (2) alter transition temperature, (3) restrict domain wall motion, (4) introduce compositional heterogeneity, (5) influence over the ionic state of the other substitutents, etc. The ionic radius concept is useful in deciding which ions are likely to be accommodated in a given lattice. Ion size, determined from the distances between the centre of ion in different compounds, is approximately constant for a given element in a wide range of compounds provided that account is taken of the charge on the ion and number of oppositely charged near-by co-ordination number. Ions of same size and same charge easily replace each other but affect the unit cell size of the parent component. According to the Goldsmith rule the dopant cation enters into the sites (A or B) in an ABO₃ type perovskite structure, if the radius of the substituted ion and replaced ion do not differ by more than 15% \[2\]. The widely accepted ionic radii of some elements used here are given in table 5.1.

In the present studies lead titanate modified with Lanthanum (La), Molybdenum (Mo) and iron (Fe) were prepared with molecular formula: Pb₁₋ₓLaₓTi₁₋ᵧMoₓFeᵧO₃ where \(x = 0.02, 0.05, 0.10, 0.15, 0.20\), and \(y = 0.02\). The compositions were prepared according to the above mentioned formula using AR grade chemicals of \(\text{PbO, TiO}_2, \text{La}_2\text{O}_3, \text{MoO}_3\), and \(\text{Fe}_2\text{O}_3\). The constituent chemicals were weighed accurately in an electronic balance with a resolution of 0.1mg. Batch of 50g of each composition was prepared. Additional 2-3% of \(\text{PbO}\) was added in each composition to compensate the loss of lead during sintering.
5.3 Mixing

It is important that constituents of a ceramic material are intimately mixed. The piezoelectric as well dielectric properties are likely to suffer if there is any lack of homogeneity. Mixing can be accomplished by a variety of machines, ranging from ball milling to heavy miller rolls. It is important that the action is vigorous enough to break up the loose aggregates.

In the present studies, wet ball milling was employed for mixing of the metal oxide powders. A ball mill is a cylindrical container that rotates on its axis and is partially filled with grounding medium. The container of about 10cm in diameter was filled with powder mixture and grinding medium (zirconia balls) greater than three times the weight of milling material. Deionised water due to its easy availability, low cost, non-toxicity and easily removable was used for liquid medium milling. The quantity of water added was sufficient to make a free flowing cream of the milling material. The container / barrel is rotated by an electrical motor with reduction gear box at about 60 rpm for 48 hours continuously.

The rotation of cylinder containing milling medium applies shearing and crushing action on material lying between the milling medium which eliminates all aggregates and reduces particle size. Ball milling is a slow process but as it is mechanically simple and robust, hence, it can be left unattended for long periods.

5.3.1 Drying

The liquid medium (de-ionised water) used in ball milling makes slurry of the powder material. The water was removed from the slurry by evaporating it in an oven (at about 100°C) fitted with air circulation system and exhaust for efficient evaporation. The slurry was placed in shallow trays with large surface area in the oven. The time required for drying depends on
the temperature of tray and depth of slurry in trays. Usually dry time of about 2 - 3 hours was required in each batch at an oven temperature at 100°C.

5.3.2. Calcination

After mixing, the material is usually calcined in the form of powder granules or loosely packed blocks. The calcination serves the following purposes.

1. It removes the water of hydration, volatile impurities if any and reduces carbonate to oxides.
2. It affects the chemical reaction among the constituent oxides to form desired solid solution.
3. As the consequences of reaction to have reduced volume shrinkage in the final firing.

Calcination sometimes also called pre-firing is treated as the advance step of mixing process because constituents interact by inter-diffusion of ions during this process. Ideally, the temperature of calcination is chosen high enough to cause complete reaction of the constituents, but low enough to prevent formation of hard aggregates which may be difficult to grind into powder. Where volatile oxides constituent form a part of the material e.g., lead oxides (PbO) the temperature must be low enough to avoid loss of these volatile oxides. Calcination is thus carried out at a temperature lower than the sintering temperature because of reasons given above and as such the calcined powder does not necessarily yield 100% final phase of the reacted constituents. The calcination is carried out by placing the mixed powders in shallow saggers in a batch or continuous kiln. The saggers are closed if any volatile constituents are present.

In the present studies the mixed powders of each composition was pressed into loosely packed blocks for easy handling during calcination. The powder blocks were calcined at 900°C for two hours in closed saggers to
reduce the loss of lead oxide. Hard aggregates formed during calcination were grounded and dried to remove moisture resulting into a free flowing powder. Calcined product is usually coarser and more abrasive than oxide raw material hence precautions against contamination during grinding were taken.

5.4 Shaping and sintering

5.4.1 Shaping

The free flowing calcined powder was granulated by forcing stiff paste of PVA binder and powder through a wire mesh of appropriate size. The primary function of the binder is to give the dry shape sufficient strength to survive the handling necessary between shaping and sintering. However, it should be possible to eliminate the binder during sintering without damaging the compact shape. The granulated powder was pressed into circular disk of 15mm diameter and ~2mm thickness by using hydraulic press at a pressure of 150MPa.

The pressure was applied slowly so that air trapped inside is allowed to escape; otherwise the air may get trapped inside the compact shape which can result in development of cracks in the compact disk. The friction between the compact and die walls must be minimum, since it will result in reduction in pressure which in turn will reduce the density of green disk. (The term ‘green’ is widely used to describe the unfired ceramic). Highly polished and punch surfaces help in reduction of friction. In order to minimize the pressure gradient on the compact disk pressure was applied on both top and bottom of the compact.

5.4.2 Sintering

In addition to composition preparation, densification of the powder into a pore-free, fully dense ceramic element is the step of processing called
sintering that is extremely critical in achieving a high quality ceramic. Sintering converts a compact powder into a denser structure of crystallites joined one another by the grain boundaries. The grain boundaries impart strength to the ceramic body typically in the range of 70-350MPa (cross breaking). Grain boundaries generally are not dense as the crystals, in the early stages of the sintering at least, and allow free diffusion of gas to and from outside the atmosphere. The energetic basis for the sintering lies in the reduction of surface energy by transferring matter from the interior of grain along the grain boundaries to adjacent pores which are eventually filled. Grain growth also takes place in parallel with densification and is energetically favoured by the reduction in area of grain boundaries. This is because that the crystal lattice has a lower free energy than the defective grain boundary region and the ratio of boundary area to volume for large grains is smaller than that for small grain. The crystallites should be larger than a certain minimum size which depends upon the composition to allow the ceramics to develop the normal piezoelectric properties. This is because, in ceramics with low grain size the ferroelectric polarization gets locked thus becomes difficult to realign or orient the domains. Such a phenomenon has seen observed in BaTiO₃ and PZT.

Sintering can be done by many methods. The oldest, most economical and simple method is conventional sintering, but it has certain limitations when it comes to achieving full density. Full density is rarely achieved in conventional sintering unless special sintering techniques are used to assist the sintering process during firing. An example of this is the use of oxygen atmosphere for sintering lead containing ceramics, such as PZT and PLZT [3].

In the present studies, the cold pressed compact disks of lanthanum modified lead titanate were sintered at different temperatures to ascertain the best sintering temperature. Fig 5.2 shows the XRD diffraction patterns of the 5 mol% lanthanum modified composition sintered at 1150°C and 1200°C for 2
hours. An unknown phase formation was observed at $2\theta = 30^\circ$ which most probably is due to “PbO” and the same disappears at sintering temperature of 1200°C. Hence, sintering temperature of 1200°C for 2 hours was found to be the best. All compositions were, therefore, sintered at 1200°C for two hours in batches. The temperature was raised @ 4°C/min. up to 1200°C and maintained at 1200°C for 2 hrs. thereafter cooled to room temperature. The sintering was carried out in closed packed alumina crucibles containing lead oxide in addition to the sintering material. Partial pressure of lead atmosphere created by lead oxide prevents excessive loss of lead from the samples. The sintered sample shrunk in size due to increase in destiny. 15 – 20% shrinkage was observed in all La-modified PT ceramics.

A small amount of excess PbO of 2-3 mol% was added in each starting composition of these ceramics. The use of excess lead oxide 1) compensates for the loss of lead during sintering and 2) forms a thin layer of liquid between the crystals of the main phase which accelerates the densification during sintering due to increased solubility. Also, the transfer of material from pore surface to the grain boundaries is more rapid where a process of solution and precipitation can occur through the medium of a liquid than in the case of diffusion through the solid and along grain boundaries.

5.5 XRD Studies

A Philips X-ray diffractometer (PW3710) was used for the X-ray diffraction studies in the present investigations. The X-rays were generated by a CuKα ($\lambda = 1.54056 \text{ Å}$) radiation. The counter is attached to the arm rotating around the same axis by an angle 2θ which is twice the angle as that of the sample rotation.

Figure 5.3 shows the XRD patterns of different lanthanum modified lead titanate ceramics. The diffraction patterns confirm the tetragonal phase formation in all the compositions [4]. It is observed from the diffraction
patterns that with the increase in lanthanum concentration the peaks (001), (110), (002) gain intensity while peaks of their counter parts (100), (101), (200) loose intensity which indicates the lattice constants (a,c) are affected by the lanthanum substitution. Increase in intensity of (001), (110), (002) etc. peaks indicate that lattice constant “c” is shrinking and decrease in intensity of (100), (101), (200) etc., indicates that the lattice constant “a” is increasing. Thus, it is evident from the diffraction patterns that lattice tetragonality (c/a) decreases with increase in lanthanum concentration.

The lattice parameters (a,c) were determined from (200) and (002) reflections using formula:

\[ d = \frac{a}{(h^2 + k^2 + l^2)^{\frac{1}{2}}} \]

Fig.5.4 shows the variation of lattice constants (c,a) and lattice tetragonality (c/a) with lanthanum substitution. It was observed that lattice constant “c” decreases and “a” increases with increase in lanthanum substitution. However, the decrease in lattice constant “c” is more than the increase in “a”. Thus, from the above observation it is seen that there is extension in unit cell along a-axis and compression along c-axis. The crystal tetragonality (c/a) ratio decreases with the increase in lanthanum concentration almost linearly (fig.5.4) Yamamoto etal [5] has reported linear decrease of (c/a) with increase in lanthanum in modified lead titanate ceramics. Decrease in c/a ratio has been reported by many researchers on different modified lead titanate ceramics [6-9]. Gradual increase in “a”, large decrease in “c” and almost linear decrease in c/a is also reported in lanthanum modified lead titanate thin films [10]. Introduction of La^{3+} or Ca^{2+} into Pb^{2+} site of lead titanate perovskite structure causes a strong reduction in “c” with not so significant change in “a” parameter as reported by Duran etal [11] which is similar to our observations.

The crystal tetragonality, c/a of pure lead titanate is 1.064 much larger than that of Barium lead titanate (BaTiO₃), c/a = 1.01. During cooling pure lead titanate ceramic after firing, the cubic phase changes to tetragonal at
curie point, and an internal stress may be induced due to phase change and cell dimension change [12]. Evidence of internal stress is the observation that sintered pure lead titanate gradually disintegrates into powder at room temperature due to mechanical breakdown [13]. The large internal stress produced due to phase transition (cubic to tetragonal) is described as $T_s \propto (\alpha - 1)$ [7]. Since the lanthanum incorporation decreases (\alpha) from its maximum value of 1.064 for pure lead titanate ceramics, the internal stresses will decrease in these lanthanum modified ceramics resulting in hard mechanically strong ceramics.

5.5.1 Density

The experimental density of the sample was calculated from the ratio of mass to volume of these samples. The theoretical density ($\rho_T$) was calculated using the equation:

$$\rho_T = \frac{Z M}{N \cdot a^2 c}$$

where $Z$ is the number of molecules in a unit cell, which for perovskite is one, $N$ is the Avogadro's number ($6.023 \times 10^{23}$ atoms/mol), $M$ is the molecular weight of the composition and "a" and "c" are the lattice parameters obtained from the X-ray diffraction patterns of the samples.

Fig.5.5 shows the effect of Lanthanum substitution on theoretical and experimental density of the samples. The theoretical density of the samples was found to decrease with increase in lanthanum concentration. Theoretical density decreases from 7.78 g/cm$^3$ for 2 mol% lanthanum composition to 7.59 g/cm$^3$ for 20 mol% lanthanum composition. Decrease in density with increase in the lanthanum concentration is due to the fact that Lanthanum atom replacing lead is lighter than the lead. So increase in Lanthanum substitution will decrease the molecular weight of the composition and thereby density. Decrease in theoretical density is observed in calcium / samarium modified lead titanate ceramics [14]. Experimental bulk density increases with increase in lanthanum substitution. Experimental density increases from 7.18g/cm$^3$ to
7.36 g/cm$^3$ for 2 mol% and 20 mol% substituted lanthanum composition respectively. The percentage experimental density increases from 92% to 97% of the theoretical density with increase in lanthanum concentration from 2 mol% to 20 mol% (fig.5.6). The increase in experimental bulk density and reduction in porosity (fig 5.6) is due to fact that increase in lanthanum content decrease the tetragonality in lead titanate ceramics, which results in reduction in internal stress [7] ($T_s \propto (1 - \alpha_a)$). Reduction in internal stress allows the crystallites in grains to accommodate more closely to form a denser microstructure, which results in reduction in porosity and increase in density. Full hundred percent density is rarely achieved with conventional sintering of ferroelectric ceramics unless special techniques are used to assist sintering process during firing [15]. With air atmosphere only density of ~97% can be achieved. But by use of oxygen atmosphere for sintering lead containing ceramics [16] density of even 99% of the theoretical density can be achieved.

5.6. Microstructure analysis

One important parameter which influences the ferroelectric, electromechanical and piezoelectric properties of a ferroelectric ceramics is their microstructure. In the present studies microstructure of modified lead titanate ceramics was studied using JEOL JSM 840 scanning electron microscope. The sample surface selected for microstructure study was smoothened by grinding with fine alumina abrasive powder in aqueous medium, and then polished with diamond paste on a rotatory polishing machine to obtain optically finished surfaces. The optically finished surfaces were etched with 5% hydrogen fluoride for 30 minutes at room temperature to reveal the grains. To make sample surface conducting a thin layer of gold (~300 A$^0$) was sputter coated on the sample. This is done to remove charge that may be deposited on the surface when electron impinges upon it.

Grain size relation with the properties of the piezoceramics is well established in the literature and continues to be studied by many
researchers. With the increased interest in the knowledge of improving material properties through microstructural control, it is obvious that the reported grain sizes and techniques used to determine grain and sizes are important to many investigations. To produce a specific grain size in a material that will achieve a desired property, the grain size determinations extracted from the literature must be valid and reproducible.

The basic technique for determination of grain size is average intercept line method (AIL) [16]. In this lines are scribed randomly across the photograph and intercepts between the lines and the grain boundaries are counted. The total number of intercept counts and total line length is computed. The average intercept length is determined as follows:

\[ \text{AIL} = \frac{L \times M}{I} \]

where \( L \) is the total length of scribed lines, \( I \) the number of intercepts, and \( M \) the magnification.

In case of polarized sections the random sections do not cut through the largest diameter of all grains on the surface, so to get actual grain size AIL is multiplied by a correction factor. [17-20]. Mendelson [18], considering the log normal distribution of grain size proposed a direct relation between grain diameter “\( D \)” and average intercept length “\( L \)” as:

\[ D = 1.7756 \left( \exp\left(-2.5 \ln \sigma^2\right) \right) L \]

where \( \ln \sigma \) is the standard deviation by log normal distribution. Hillert [21] by assuming distribution function \( D=1.57L \) and using log of normal distribution function [22]:

\[ D = 1.558L \]

A good review of various correction factors is given by Mendelson [18]. Chermant et al [23] and Mendelson [18] have proposed correction factors of \( 4/\pi \) and and 1.56 respectively.

In the present studies on grain size of Lanthanum modified lead ceramics the grain size was determined by average intercept line method. Three to four sights were photographed in each sample and in each photomicrograph 10-12 index lines were scribed covering the entire micrograph.
The grain size "L" was determined by averaging the individual determination, no correction factor was used.

Fig 5.7 shows the photomicrographs of the lanthanum modified lead titanate ceramics. The micrographs show well defined grains and grain boundaries. The grain size is found to be increase with the increase in lanthanum substitution (fig 5.8) and varies from 1\( \mu \)m for 2 mol% lanthanum composition to 2.83 \( \mu \)m for 20 mol% composition. The porosity is observed to decrease with increase in Lanthanum substitution, porosity is minimum for sample with highest grain size (20 mol% La) and the grains appear fit the more competitively by adjusting the grain boundaries. Reduction in tetragonality [7] and its role played in microstructure compaction is attributed to reduction in porosity. Fine grain size does not seem to be a necessary condition for high dense ceramics since in our ceramics density as well as the grain size increase with increase in lanthanum content, and such an observation is also reported in the literature [24]. It has been reported that in ferroelectric ceramics to produce highly dense and hard ceramics either size of crystals or tetragonality should be reduced by modifications. In our ceramics the reduction in tetragonality seems to be responsible for dense and strong microstructure obtained in samples containing higher lanthanum content. Influence on the grain size due to additives is also reported [14,25].

5.7 Conclusion

Lanthanum modified lead titanate ceramics were prepared by solidstate reaction. Suitable sintering temperature is found to be 1200\(^\circ\)C for 2 hours. X-ray diffraction patterns confirm the single phase formation in all samples. Lattice parameters determined from X-ray diffraction studies show that lattice constant "c" decreases sharply and gradual increase in lattice constant "a" with the increase in lanthanum substitution. Lattice tetragonality (c/a) reduces almost linearly with increase in Lanthanum substitution. Theoretical density is found to decrease with the increase in Lanthanum
content which is reasonable because Lanthanum is lighter than lead. Experimental density is found to increase from 92% to 97% of the theoretical density. Increase in experimental density is attributed to reduction in internal stress by decrease in tetragonality which helps producing a compact microstructure and reduction in porosity. The grain size is found to increase from 1 \mu m to 2.83 \mu m with increase in lanthanum content from 2 mol\% to 20 mol\%.
References


Table 5.1. Ionic radii of some elements

<table>
<thead>
<tr>
<th>Ion</th>
<th>Radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb$^{2+}$</td>
<td>1.20</td>
</tr>
<tr>
<td>La$^{3+}$</td>
<td>1.15</td>
</tr>
<tr>
<td>Ti$^{4+}$</td>
<td>0.68</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>0.76</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>0.64</td>
</tr>
<tr>
<td>Mo$^{5+}$</td>
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</tr>
<tr>
<td>Mo$^{4+}$</td>
<td>0.64</td>
</tr>
</tbody>
</table>
Fig. 5.1 Various steps in processing of ceramics by conventional technique
Fig. 5.2 XRD pattern of 5 mol% lanthanum modified lead titanate ceramics (a) Sintered at 1150 °C (b) Sintered at 1200 °C.
Fig. 5.3 Continued on the next page.
Fig. 5.3 XRD pattern of lanthanum modified lead titanate ceramics sintered at 1200 °C.
Fig. 5.4 Effect of lanthanum substitution on lattice constants (c, a) and lattice tetragonality (c/a)
Fig. 5.5 Effect of lanthanum substitution on density
Fig. 5.6 Effect of lanthanum substitution on porosity and percentage theoretical density.
Fig. 5.8 Grain size Vs. lanthanum concentration.