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Synthesis & Characterisation of Ferroelectric Ceramics

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Lead Zirconate Titanate (PZT) and lead Lanthanum Zirconate Titanate (PLZT) have been prepared by following dry route method. XRD of the material gives the structure of ceramics its dielectric constant was measured. The recent developments in the field of ferroelectric ceramics such as medical ultrasonic composites, high displacement piezoelectric actuators, photostrictors and integrated circuits have served to keep the industry young amidst its growing maturity.

Key words : *PZT, PLZT, XRD.*

Introduction : Ferroelectric ceramics were born in the early 1940s with the discovery of the phenomenon of ferroelectricity as the source of the unusually high dielectric constant in ceramic barium titanate capacitors (Haerting 1999). Since that time they have been the heart and soul of several multibillion dollar industries, ranging from high dielectric capacitors to later developments in piezoelectric transducers, positive temperature coefficient devices and electrooptic light valves.Material based on two compositional systems, barium titanate and lead zirconate titanate have dominated the field throughout their history. The time period is from the early 1800s to the present involving events from the early work on single crystal Rochelle Salt. Since the discovery of ferroelectricity in single-crystal materials (Rochelle Salt) and its subsequent extension into the realm of polycrystalline ceramics (barium titanate) during the early to mid- 1940s, there has been a continuous succession of new materials and technology developments that have lead to a significant number of industrial and commercial applications that can be directly credited to this most unusual phenomenon. Among these applications are high dielectric-constant capacitors, piezoelectric sonars and ultrasonic transducers, radio, gas ignitors, etc. The history of discovery of ferroelectricity (electrically switchable spontaneous polarization) is a fascinating one that extends as far back as the mid- 1600s when Rochelle salt was first prepared by Elie Seignette in La Rochelle, France, for medicinal purposes. However, it was approximately 200 years before this water-soluble crystalline material would be investigated for its pyroelectric (thermal polar) properties, another half century before its piezoelectric (stress-polar) properties would be uncovered, and finally another 40 years would pass before ferroelectricity would be first discovered by J. Valasek in this material. Rochelle salt was a popular material in these initial studies, because it was readily available and easily grown as large single crystals of excellent optical quality, but its water solubility eventually lead to its disuse in later years.
(Valasek J (1921), Pillau S.O. 2003)

Stoichiometric Calculations :

Stoichiometry is the calculation of the quantities of reactants and product involved in a chemical reaction. It is based on the chemical equation and on the relationship between mass and moles. A chemical equation can be interpreted as follows:

$N_{2(g)} + 3H_2(g) \rightarrow 2NH_3(g)$

1 mol N_2 + 3 mol H_2 → 2 mol NH_3 (molar interpretation)

Stoichiometric details

In dry route method, oxide of divalent materials, monoxides of lead and acetone for oxygen are taken in stoichiometric proportion in a solid form and milling in a agate mortal pestle for about 8 hours. This sample is a new class of ferroelectrics of octahedral ABO_3 group.

(a) Name of sample prepared – PZT (Lead Zirconium Titanate) $PbZr_{0.65}Ti_{0.35}O_3$

Molecular fraction required for 30gm-

Chemical used-1. Zirconium Dioxide (ZrO_2), Molecular weight-123.22 gm /mole, Purity > 97%, (company- Loba chemie). 2.Lead Monoxide (PbO), molecular weight- 223.19 gm/ mole, Purity>98%,

(company- Nice), 3. Titanium Dioxide (TiO_2), Molecular Weight- 79.00 gm/ mole, Purity>99%, (Company- Loba chemie).

Weight taken according to stoichiometric calculation, ZrO_2- 7.254g, PbO- 20.21g and TiO_2- 2.53g

(b) Name of the sample prepared – PLZT(PZT doped with Lanthanum)

PLZT-11/65/35

$Pb_{0.89}La_{0.11}Zr_{0.65}Ti_{0.35}O_3$

Weight taken according to the stoichiometric calculations , ZrO_2-7.4166g, PbO-18.409g, TiO_2-2.5893g, La_2O_3- 3.3187g

(c) Name of the sample prepared – PLZT(PZT doped with Lanthanum)

PLZT-9/65/35

$Pb_{0.91}La_{0.09}Zr_{0.65}Ti_{0.35}O_3$

Weight taken according to the stoichiometric calculations , ZrO_2-7.3915g, PbO-18.74g, TiO_2-2.580g, La_2O_3- 2.706g

Experimental Dry Route Method :

Ferroelectric ceramics are traditionally made from powders formulated from individual oxides; however the newer electrooptic materials and some of the PTC (positive Temperature co-efficients) ceramics utilize chemical coprecipitions or hydrothermal techniques. The processing method that selects to prepare the powders depends, to a large extent, on cost, but even more important is the end application. Understandably, electrooptic ceramics require higher-purity, more homogenous and higher –reactivity powders than do the piezoelectric ceramics because inhomogenities can be detected optically much more easily than electrically As a result different powder techniques have evolved in the two cases. Piezoelectric ceramics continue to be prepared in the most economical form mixed from oxides process, whereas the optical ceramics utilize specially developed chemical coprecipitation processes involving liquid inorganic or organometalic precursors. Although not yet fully achieved, the trends in this area are towards the development of on unified process that meets the objectives of both types of material. There is a commonality in these objectives, because the more recent piezoelectric devices demand higher-quality material (essentially zero porosity) and the electrpooptics require a more economical process.

A flowchart describing the essential steps for both the MO (Hippel A. Von (1950)) (mixed oxides) and CP (Citrate Precursor) process is given in figure1. There are many steps that are common to both methods. The essential differences between the two methods occur in the powder forming and densification stages. In the MO methods, this very simply consists of wet milling (slurry form) the individual oxides that decompose to the oxides during calcining (a high- temperature solid state chemical reaction) at 800˚C - 900˚C about two to three hours.

Ball milling of the calcined material is neccessary for both types of powders to produce the required chemical and optical homogeneity. This is the very critical step in the process, because too little milling does not produce the necessary homogeneity, and over milling increases the likelihood of contamination leading to optical scattering. A common practice is to use a plastic- lined mill with high- density media (alumina or zirconia balls) and a non polar, nonflammable milling liquid, such as trichloro ethylene or Freon TF, for the electrooptic materials; however, distilled water is a better liquid for piezoelectrics from a cost and environmentally preferred standpoint. Depending on a particular powder characteristics, milling times may vary from 24 to 48 hours. The milled powder are then thoroughly dried, mechanilly broken up, homogenized in a V- blender, and stored for further processing.

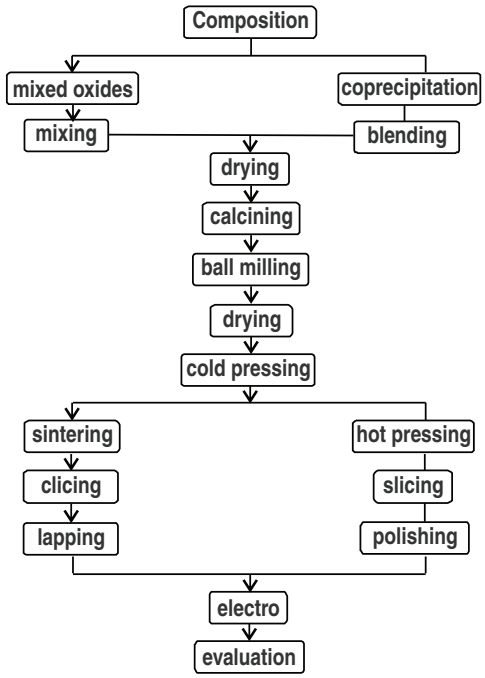

Figure 1: Flow chart for processing of piezoelectric and electrooptic ceramics. The highlighted Dry route method of preparation is followed by us.

Result and discussion :

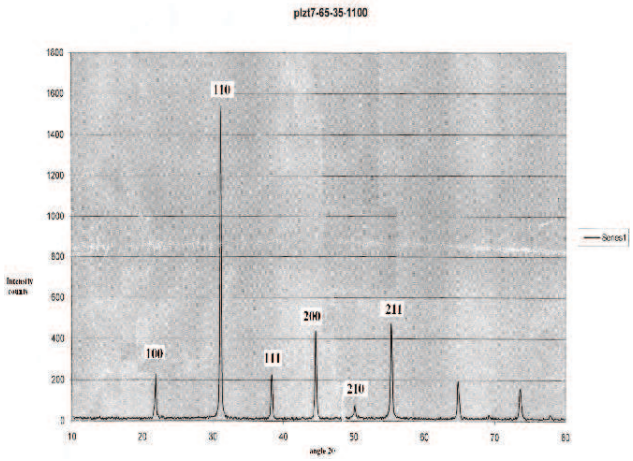

Fig. 2 Graph shows the XRD patten of the ferroelectric sample show will defined sharp peak with (h, k, l) values.

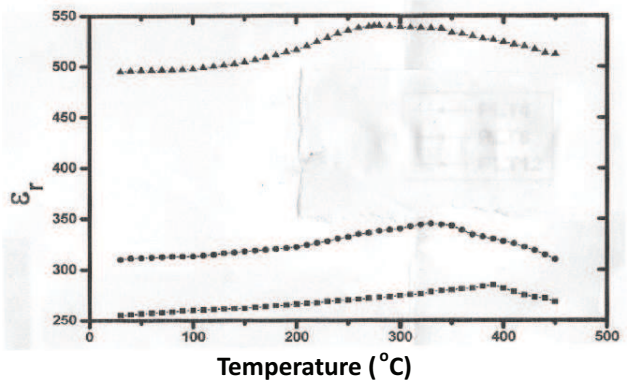

Fig. 3. Graph showing variation of dielectric constant with temperature for different ferroelectrics

Conclusion and future prospects :

Present market trends continue to show that the future for ferroelectric ceramics is bright and continues to get even brighter as the transition is made from passive to electrically active “smart” and “very smart” materials. In this regard, a smart material senses a change in the environment and, using an external feedback control system, makes a useful response, as in a combined sensor/actuator ceramic. A very smart material senses a change in the environment and response by reacting and tuning one or more of its properties to optimize its behaviour. An example of the smart type is a piezoelectric ceramic and of the very smart type is a non linear, electrostrictive relaxor. Multifunctionality is a key concept of these materials that will be exploited with all the ingenuity that design engineers can muster (Newnham R.F. 1996).

In the future, more and more applications for non-linear, electrostrictive relaxor materials, such as PMN and PLZT, will emerge as the relentless drive towards miniaturization and integration continues. Indeed, this very trend will also encourage more materials research efforts to develop better ferroelectric and electrostrictive ceramics.

Brought on by the need for higher- capacity memories, ex-direction set a few years ago for ferroelectric films is expected to continue and broaden in scope. Thin- and thick- film technologies alike will also share in the current trend toward composite and graded layers of the same material, are now achievable with most conventional film deposition processes on a micro scale, and this will be more common place in the future on a nano scale (Scott J.F. 1998).

Because thin- and thick- film technologies generally do not limit, but rather enhance, the portfolio of materials to be used in various applications, it is expected that a variety of materials will continue to be studied, but there will be a narrowing down to fewer serious candidates of known behaviour in order to bring the devices in development to the market place. Undoubtedly, BST, PZT, PLZT, PMN and SBT are destined to be leading candidates in this arena. Regarding film deposition techniques, at this stage in the development of the films, it is very difficult to judge which film deposition technique will emerge as the favourite; however, because several methods have been used successfully, it is most likely that several methods will survive, and a specific methods selected will be dictated by cost and the application.

Because of their intrinsic dielectric nature and large number of interactive and electrically variable properties, ferroelectric ceramics are destined to figure prominently in the future. Bulk, thick- film, and thin- film forms of these materials have now proved their worth, and, together, they will constitute a strong portfolio of materials for future applications in electronics.

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