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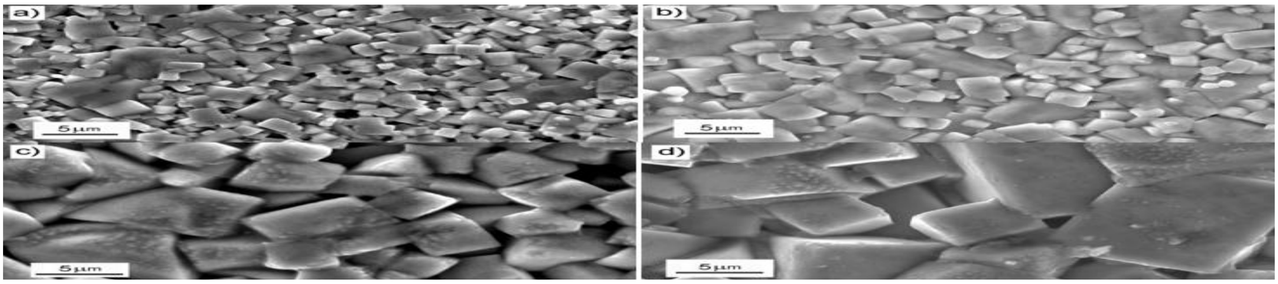


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STRUCTURAL CHARACTERIZATION OF CALCIUM MODIFIED LEAD TITANATE CERAMICS

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ABSTRACT

The paper deals with the physical properties of lead titanate (PT) sample with additives. The modification of this sample was carried out by adding calcium in proportion of 5 to 15mol%. The samples in bulk form were synthesized by utilizing traditional method of solid state synthesis. The properties like structural analysis, and grain size determination were studied for the lead titanate sample and for the calcium modified lead titanate (PCT). The phase identification, characterization and microstructural analysis is discussed in this paper.

KEYWORDS: Solid state synthesis, lead calcium titanate and ferroelectric ceramics.

1. INTRODUCTION

Ferroelectricity is a phenomenon which was discovered in 1921. The name refers to certain magnetic analogies, though it is somewhat misleading as it has no connection with iron (ferrum) at all. Ferroelectricity has also been called Seignette Electricity, as Seignette of Rochelle Salt (RS) was the first material found to show ferroelectric properties such as a spontaneous polarization on cooling below the Curie point, ferroelectric domains and a ferroelectric hysteresis loop. A huge leap in the research on ferroelectric material came in the 1950's, leading to the widespread use of Barium Titanate (BaTiO3) based ceramics in capacitor applications and piezoelectric transducer devices.

Since then, many other ferroelectric ceramics including Lead Titanate ($PbTiO_3$), Lead Zirconate Titanate (PZT), Lead Lanthanum Zirconate Titanate (PLZT), and relaxor ferroelectrics like Lead Magnesium Niobate (PMN) have been developed and utilized for a variety of applications. With the development of ceramic processing and thin film technology, many new applications have emerged. The biggest use of ferroelectric ceramics have been in the areas such as dielectric ceramics for capacitor applications, ferroelectric thin films for non volatile memories, piezoelectric materials for medical ultrasound imaging and actuators, and electro – optic materials for data storage and displays [1-12]. In this paper attention has been focused on the study of the ferroelectric materials: pure and Ca modified $PbTiO_3$ with perovskite structure.

2. EXPERIMENTAL PROCEDURE

Synthesis of pure Lead Titanate [$PbTiO_3$]

The starting materials were commercially available Lead Carbonate, $PbCO_3$ (GR) and Titanium dioxide, TiO_2 (GR) with 99% purity. The two oxide powders exhibited an average particle size in the range of 3.0 to 5.0 µm. $PbTiO_3$ powder was synthesized by the solid state reaction of thoroughly ground mixtures of $PbCO_3$ and TiO_2 powders that were milled in the required stoichiometric ratio. The milling operation was carried out for 5h. High purity (99%) agate mortar was used as the milling media. After milling powder sample was calcinated at 900°C for 5h in silica crucible, in order to investigate the formation of $PbTiO_3$. The calcined powder was cooled to room temperature and mill in the required stoichiometric ratio. $PbTiO_3$ powder was subsequently examined by room temperature. $PbTiO_3$ powders were conventionally synthesized by solid state reaction between $PbCO_3$ and TiO_2 at 900°C. The overall reaction for the $PbTiO_3$ formation while heating equi - molar $PbCO_3$ and TiO_2 mixture is

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

Synthesis of Lead Calcium Titanate (PCT)

In order to carry out the research on lead calcium titanate (PCT) has been synthesized by utilizing traditional method of solid state synthesis. Stoichiometric amounts of high purity calcium oxide, CaO (all over ~ 99.9% purity) were carefully weighted and was doped in a proportion of 5, 10, 15 mol% with synthesized Lead Titanate ($PbTiO_3$) powder. This powder mixture was mixed in an agate mortar for 2 hrs. In order to reduce the impurities and obtain homogeneity of the final compound the samples were calcined in silica crucible at 750°C for 5 hrs followed by furnace cooling. The calcined material was once again ground thoroughly in required stoichiometric ratio. The pressure of 70 kg/m2 for 3 min was employed to the sample in the hydrostatic conditions using hydraulic press. The pellets of diameter 10mm, thickness ~ 2mm and weight ~ 1 gm of this well dried powder were prepared. Since the green samples include the organic additive that must be completely removed to avoid the undesirable effects on the properties of the final products, slow heating rate (1oC/min) is required until temperature reaches 400°C around which the most amount of PVA decomposes . After 3 hours of holding at that temperature to complete the organic burnout, lead calcium titanate samples were then heated up to 850°C in air with the rate of 5°C/min for the solid state sintering process. And then the sample was cooled through air.

3. RESULTS AND DISCUSSION

Characterization Plots

The phase identification and quantification was performed of the starting oxides mixture and calcined samples by X – ray powder diffraction method on X –Ray Diffractometer (D – 8 Advance Fruker axs) over a wide range of Bragg angles ($20^o \leq 2\theta \leq 80^o$) at room temperature. Fig. 1 shows the XRD spectra of the pure lead titanate calcined at temperature 850°C. Using Bragg's condition (λ = 1.5406Å), interplaner spacing d (calculated with refined cell parameter) of (h k l) planes was calculated, and compared with those of observed/calculated values. The best agreement between dobs and dcal value. The best agreement between d_{obs} - d_{cal} value (i.e. $\sum\Delta d$ = (d_{obs} - d_{cal}) = minimum) was found as shown in table 1.

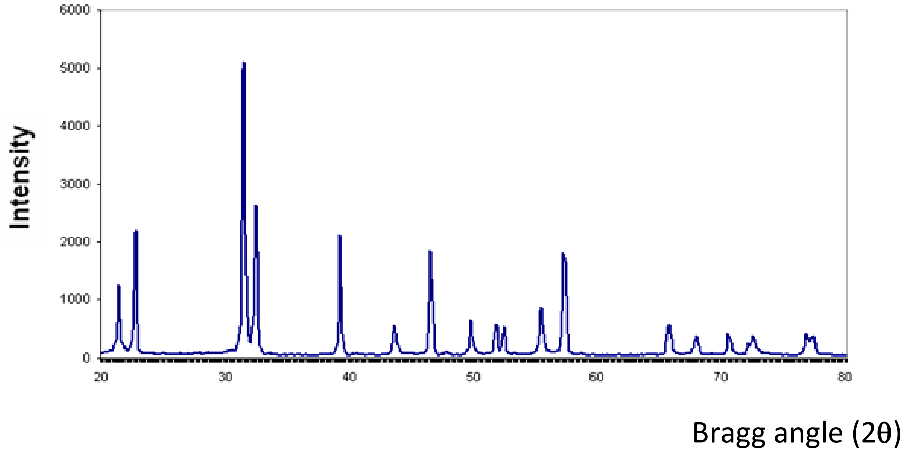


Fig. 1: X-Ray diffraction of pure lead titanate ($PbTiO_3$)

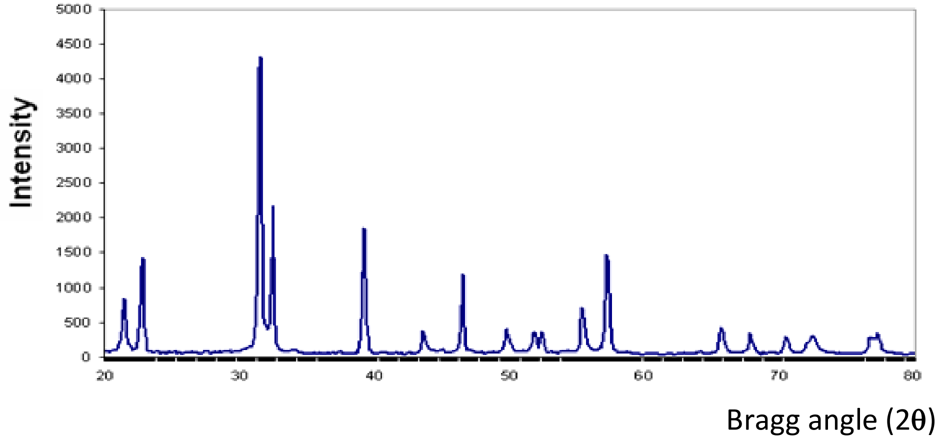


Fig. 2: X-Ray diffraction of modified lead calcium titanate (calcium doped in 5 mol% in pure lead titanate)

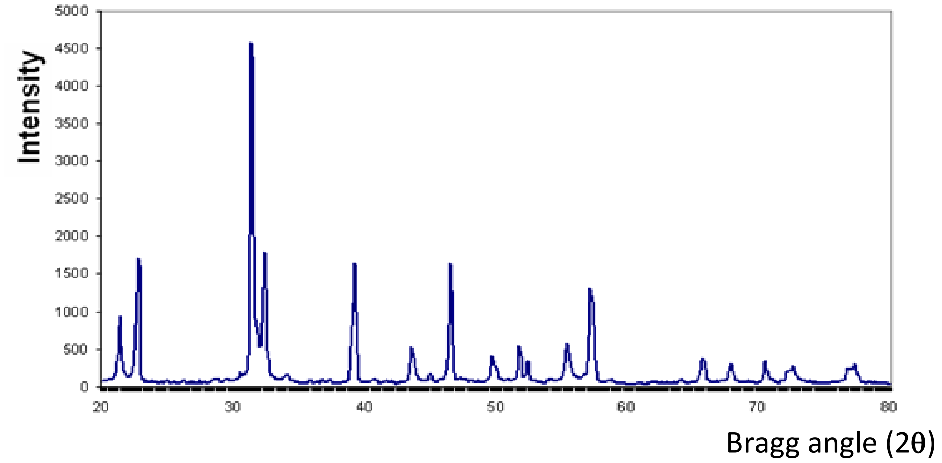
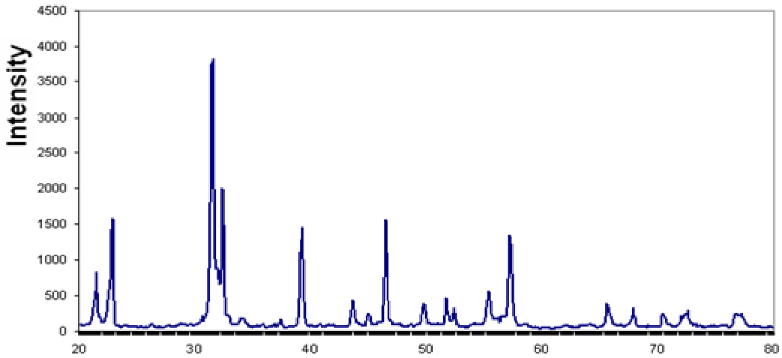


Fig. 3: X-Ray diffraction of modified lead calcium titanate (calcium doped in 10 mol% in pure lead titanate)



Bragg angle (2θ)

Fig. 4: X-Ray diffraction of modified lead calcium titanate (calcium doped in 15 mol% in pure lead titanate)

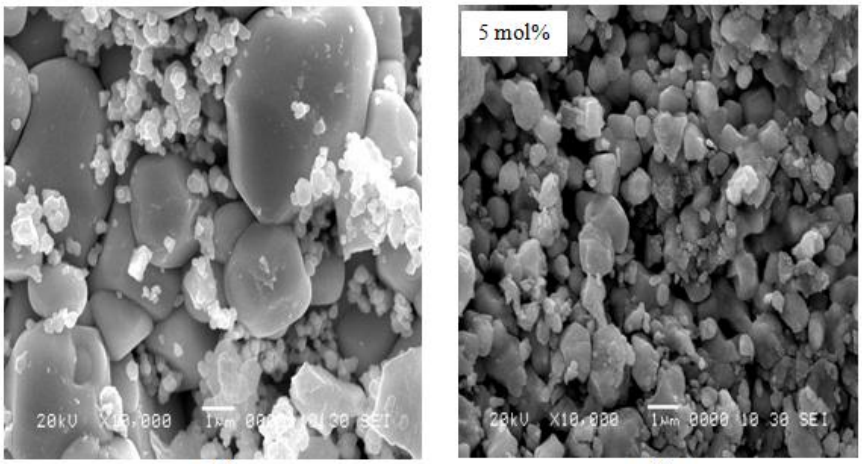
X – ray analysis on powder sample calcined at temperature 850^{o}C was studied, the structure of sample lead titanate to be tetragonal with a = 3.9015 Å; c = 4.1486 Å and (c/a = 1.063). The a and c parameter are in good agreement with values in the literature [13].

Table 1: X- ray powder data (Observed and Calculated)

hkl	Observed Data	Calculated Data
	d_{obs} $\overset{o}{A}$	d_{cal} $\overset{o}{A}$
001	4.150	4.149
100	3.899	3.897
101	2.842	2.838
110	2.758	2.761
111	2.297	2.296
002	2.076	2.074
200	1.950	1.954
102	1.833	1.833
201	1.765	1.767
210	1.744	1.745
112	1.658	1.657
211	1.607	1.609
202	1.421	1.420

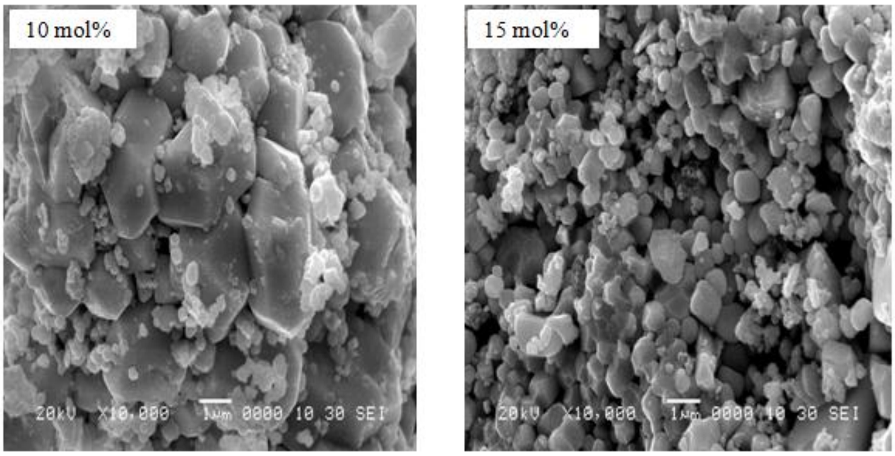
The crystallographic structure of the PCT sample for various compositions has been studied by XRD. Fig.2, 3 and 4 shows the effect of varied Ca concentration (5, 10 and 15 mol%). The pattern shows well resolved peaks in all case. It was found that the increase in concentration of Ca decreases the intensity of the maximum resolved peaks [14, 15]. XRD analysis shows all the samples to be single phase with tetragonal structure. The lattice parameter (c and a), tetragonality (c/a) were calculated. It is seen that there is no change in ‘c’ and ‘a’ values. As per published literature c/a ratio, which is a measure of crystal tetragonality, is remain same in this case [16]. This difference may be due the change in the concentration of dopant and the method employed for synthesis.

Microstructural Analysis



(a) (b)

Fig. 3(a), 3 (b): Scanning electron microscopy of pure lead titanate sample, 5 mol% of calcium doped in pure lead titanate.



(c) (d)

Fig. 3(c), 3 (d): Scanning electron microscopy of 10 and 15 mol% of calcium doped in pure lead titanate.

The scanning electron micrographs of sintered samples show the uniform distribution and densely packed grains over the entire surface. The average grain size of the sample determined by using Contrell's method [17] was found to be in the range of 1 – 2 µm. The microstructural analysis showed that as the Ca concentration increases, grain size first increases from 1.04 µm to 1.52 µm for 5 mol% to 10 mol% followed by the decrease up to 0.99µm for 15 mol% as shown in table 2 [18 -19]. This may be due to solubility limit.

Table 2: Variation of Grain size with different mol%

mol%	Average Grain Size (µm)
0 (Pure Lead Titanate)	1.04
5	1.18
10	1.52
15	0.99

4. CONCLUSION

The Lead Calcium Titanate (PCT) samples have been successfully prepared in bulk form by solid state synthesis method. The structural analysis and grain size determination have been analysed using x-ray diffraction and microstructural analysis techniques. The value of ‘a’ and ‘c’ have been obtained. The method employed for characterization reduces the porosity of pure lead titanate.

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