Structural Phase Transition In Ca$_{(X)}$Pb$_{(X-1)}$TiO$_3$ Nanoparticles Prepared By Wet Chemical Route

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Abstract: Solution of molar proportion of precursors Lead Nitrate [Pb(NO$_3$)$_2$], Titanium Tetra Chloride [TiCl$_4$] and Nitric Acid [HNO$_3$] and Calcium Nitrate [Ca(NO$_3$)$_2$] is stirred for 1 h at 110°C by using wet chemical route. The white raw powder so obtained is then calcined at 600°C, 700°C and 800°C to obtain nanoparticles of Calcium doped Lead Titanate (PCT). X-ray diffraction [XRD] studies of the 0.6 molar calcium concentration in lead titanate make out 13 nm nano-crystallites at 600°C calcination. Around 0.5 molar concentration of Calcium in Lead Titanate phase transition from Tetragonal to pseudo-cubic structure occurs.

Keywords: PCT; Wet Chemical Route; Phase Transition.

Introduction And Experimental

Perovskite systems (ABO$_3$) have been studied widely for its B site substitutions [1-2]. Substitution for A site by Pb$^{2+}$ maintains the perovskite crystal structure. Its behavior at A site can be modified by operating Pb$^{2+}$ and iso-valent additives Ca$^{2+}$, Ba$^{2+}$, Cd$^{2+}$, Sr$^{2+}$, etc. and many new characteristics and applications with different sizes can be realized [3-5]. Mainly these applications include both fabrications of the fine ferroelectric nano-particles. Therefore, the study of size effects on the structure of ferroelectric nano-crystals has recently become important. Structural phase transition in these materials has not been clarified with extensive work even [6]. In this progress wet chemical route is reported here to aim at structural phase transition by using Ca$_{(X)}$Pb$_{(X-1)}$TiO$_3$ system. Solution of molar proportion of precursors Lead Nitrate [Pb(NO$_3$)$_2$], Titanium Tetra Chloride [TiCl$_4$], Nitric Acid [HNO$_3$] and Calcium Nitrate [Ca(NO$_3$)$_2$] is stirred for 1 h at 110°C. Powder is then calcined at 600°C, 700°C and 800°C to obtain nanoparticles of Calcium doped Lead Titanate. The phase transition of powders is studied from XRD. Pure powders are then labelled as PT & PCT with calcium doping.

Results And Discussion

Structural Phase Transition In Ca$_{(X)}$Pb$_{(X-1)}$TiO$_3$: Figure 1 shows XRD pattern of calcium doped lead titanate calcined at 600°C. The formation of tetragonal phase is confirmed from experimental peaks, compared and indexed from JCPDS file 74-2495 and 43-0303. Debye-Scherer equation [7, 8] is used to calculate the
average crystallite size. The plot of calculated average nano-crystallite size, effect of temperature and PCT is presented in Figure 2. It is observed that for undoped lead titanate crystallite size is higher, the lowest value of 13 nm is observed for 0.6 moar concentration in PT calcined at 600°C. The crystallite size appears to be following a decreasing trend within error limit. Thus, the observation shows that Ca may act as grain growth inhibitor [9].

![Figure 1: Indexed XRD patterns of lead titanate doped with calcium calcined at 600°C](image1)

At the room temperature, nano-crystalline PCT powder has major peak at (101) which belongs to the tetragonal phase. Experimentally calculated values of c/a at different calcination temperatures for the PCT are presented in Figure 3. c/a ratio attains a maximum at 0.3 mole concentration of calcium and for higher concentration it decreases. Thus, the calcium doping initially improves the tetragonality but on increasing calcium concentration, structure approaches to slightly tetragonal structure called pseudo-cubic [10-12]. It may help the study of its application in ferroelectric.

The major diffraction peaks corresponding to diffraction planes 101, 110 and 100 ascribed to the tetragonal PbTiO$_3$ as per JCPDS card file in experimental data has been taken for the reference calculations of the phase conversion of the calcium doped lead titanate. The % relative phase conversion of the PCT data at different calcination temperatures to that of reported in JCPDS card for PT is presented in figure 4. It is estimated for major peak position intensities from XRD results using the equation [13].

![Figure 3: c/a ratio vs calcination concentration](image2)

![Figure 4: % Relative phase conversion ratio w.r.t. calcium concentration](image3)

Conclusions:

Successfully, calcium doped lead titanate with crystallite size of 13 nm for 0.6 moar Calcium concentration calcined at 600°C is synthesesised. The phase transition in Lead Titanate with calcium doping is studied from lattice anisotropy and justifies for around 0.5 molar calcium contents in lead titanate to get phase transition from tetragonal structure to pseudo-cubic. The percentage of relative phase conversion is also studied and reported.
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