Effect of Iron Substitution on Structure and Optical Properties of Nanocrystalline CaTiO₃

A. Bandyopadhyay[1], S. Mondal[1], M. Pal[2], U. Pal[3], and M. Pal[1,a]

[1]Department of Physics, The University of Burdwan, West-Bengal, 713 104, India

[2]Department of Physics, Sarojini Naidu College, Kolkata, India

[3]Instítuto de Física, Universidad Autónoma de Puebla, Apdo. Postal J-48, Puebla, Pue. 72570, Mexico

[a]email: mrinalp@yahoo.com (corresponding author)

Abstract. Nanocrystalline CaTiO₃ powders doped with Fe₂O₃ have been prepared using a soft chemical route. Precipitation of CaTiO₃ nanocrystals has been studied by monitoring the exothermic peak in their DSC spectra. The crystal growth temperature of the samples depends on the concentration of iron. Surface morphology, crystal structure, optical and electrical properties of the nanostructures are investigated. X-ray diffraction study shows that the as-prepared powders are amorphous in nature and CaTiO₃ phase formation starts at around 500 ^{0}C. Rietveld analysis revealed that the particle size of iron substituted CaTiO₃ is in nanometer range. Optical bandgap of the nanostructures varies from 4.3 to 3.7 eV for the variation of iron concentration from 0.05 to 0.2 mole %.

Introduction

Perovskite based on titanate are interesting materials for room temperature applications mainly due to their dielectric properties [1]. Mineral CaTiO₃ is the founder father of perovskite-structure family. Due to polar soft mode, CaTiO₃ does not exhibit a ferroelectric phase transition and belongs to quantum paraelectric or incipient ferroelectric group. It is widely used in electronic ceramic materials and in immobilizing radioactive waste [2]. The phase transition of CaTiO₃ has been studied extensively and is reported to undergo structural changes from orthorhombic to cubic symmetry [3-6]. However, there are contradictions over the number of existing phase in CaTiO₃, which is an unresolved issue. It may vary from two to four according to the reports available so far.

It is well known that partial substitution of Ti^{4+} by Fe^{3+} in CaTiO₃ leads to the formation of oxygen vacancies and becomes a mixed oxygen ionic and electronic conductor [7]. Therefore, iron substituted CaTiO₃ is a prospective candidate for application as a ceramic membrane for oxygen separation [8]. Also the presence of iron in CaTiO₃ has an effect on its high temperature phase transformation [9]. Nanocrystalline materials have attracted much attention during last two decades, and it is well known that all the physical and chemical properties changes drastically when size goes down to nanometer range [10,11]. Most of the published works have been concerned with the structural changes of CaTiO₃ either in bulk or in thin film form. Available informations on the structural phase change and other properties of doped nanocrystalline CaTiO₃ are limited, and not

systematic. In the present work, iron doped nanocrystalline $CaTiO_3$ are prepared using a soft chemical rout, and the effects of iron substitution on their growth and optical properties have been studied.

Experimental

Four samples of iron substituted $CaTiO_3$ having composition $CaTi_{(1-x)}Fe_xO_{3-\delta}$ ($0.05 \leq x \leq 0.02$) have been prepared in nanocrystalline form. A soft chemical route has been utilized to prepare nanocrystalline $CaTiO_3$. This route has the advantages like low processing temperature, better homogeneity, etc. Reagent grade $CaCO_3$, tetraisopropylorthotitanate $[(C_{12}H_{28}O_4)Ti]$ and $Fe(NO_3)$ have been used as precursors. Separate sols of the individual precursors having weighed amounts were prepared with the addition of 10 ml distilled water and 10 ml ethanol. Each solution was stirred for 1h after adding two drops of nitric acid so that the pH of the solutions remained in the acidic range. These separate solutions were mixed together and the grand mixture was stirred again for 2 h. The resulting mixture was then subjected to gelation for three days and then evaporated to dryness to obtain as-prepared sample in powder form [12]. The dry powders were annealed up to 600^oC with a step of 100^oC in ordinary air atmosphere in a precisely controlled high temperature furnace (Thermolyne type 46100).

A differential scanning calorimeter (Shimazdu DSC-60) has been used for the thermal study of as-prepared samples. The crystalline phases present in the different annealed samples were identified from the diffractograms taken in a Rich Philips PW 1710 X-ray diffractometer using $CuK\alpha$ radiation. Detailed structural and microstructural characterization was done using modified Reitveld method employing the software MAUD [13]. The optical absorption spectra in the range 200 - 800 nm for all the samples were carried out on a Hitachi spectrophotometer (model U3410) by dispersing the annealed powder samples in ethanol. Nicolet Magma-IR (750, Series II) with a resolution of 1 cm $^{-1}$ has been used to check the vibrational spectra of all the annealed samples.

Results and discussion

The DSC curve of as-prepared samples shows two sharp exothermic peaks at one around 150^oC and the other around 500^oC. The first exothermic peak may be due to the decomposition of acids, which were used during the sol preparation. The second sharp exothermic peak is associated to the crystallization of $CaTiO_3$ phase. Nature of DSC curve is same for all the samples. Figure 1 depicts the variation of estimated crystal growth temperature with doping concentration. It is observed that the crystalline temperature decreases with the increase of Fe_2O_3 content. This indicates that Fe_2O_3 is acting here as a nucleating agent. Growth of $CaTiO_3$ phase at the estimated crystallization temperature was later confirms by FTIR and XRD studies.

XRD patterns of all the as-prepared samples revealed only a broad diffuse hump around low angle region, indicating clearly the amorphous nature of the as-prepared samples. The as-prepared samples remain amorphous and precipitation of $CaTiO_3$ phase starts at around 500^oC. Fig. 2 shows the XRD patterns of annealed sample doped with 0.1 % Fe_2O_3 at two different temperatures. The peaks in the XRD pattern exhibit the formation of single phase $CaTiO_3$ without any trace of Fe_2O_3. Absence of any peak of Fe_2O_3 indicates the complete dissolution of Fe_2O_3 in $CaTiO_3$ at least up to the doping concentration of 0.2 mole %. With the increase of annealing temperature, XRD peaks become sharper and more intense, indicating the enhanced crystallinity of the powders.
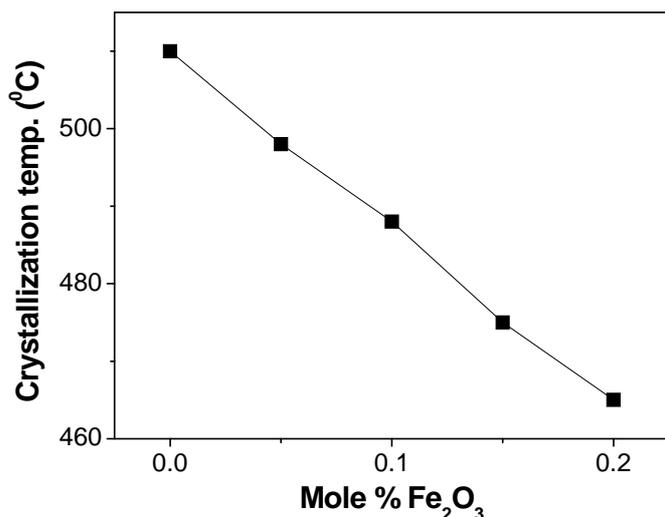
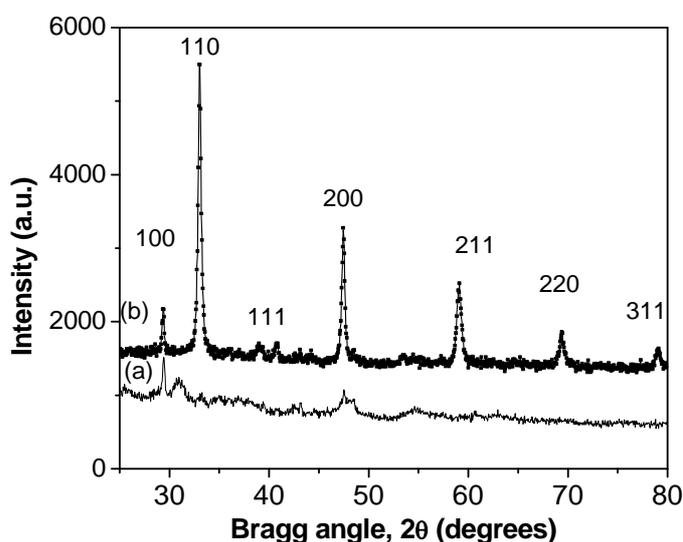**Figure 1.** Variation of estimated crystallization temperature with doping concentration.

Figure 2. XRD patterns of the sample doped with 0.1 % Fe_2O_3: a) annealed at 500^oC for 30 min. and b) annealed at 600^oC for 30 min.

The structure refinement and size-strain determination of annealed samples were carried out simultaneously by adopting the modified Rietveld method [14]. We have annealed all the samples at 600^oC for 30 min. and performed the Rietveld analysis. The variation of particle size for the annealed samples with the doping concentration is presented in Fig. 3.

Fig. 4 shows the FTIR spectrum of the 0.1% Fe_2O_3 doped sample annealed at 600^oC for 30 min. The sharp band around 3500 cm^{-1} is due to the stretching of O-H bond and confirms the low H_2O content in the sample. The vibrational band (small and wide) in the low wavenumber region is attributed to M-O (M = Ti /Ca) bond. The band at around 465 cm^{-1} (marked as A in the inset) can be attributed to the systematic distortion from ideal cube symmetry to orthorhombic structure for $CaTiO_3$. The sharp peak at around 575 cm^{-1} (marked as B in the inset) can be attributed to the Ti-O stretching mode. Another band at around 875 cm^{-1} (marked as C in the inset) is due to the vibration of Fe-O bond. The presence of these several bands confirms the formation of $CaTiO_3$ phase doped with Fe_2O_3 in the annealed samples. The wide and narrow peaks attributed to the nanometer dimension of the samples. There was no such detectable shift of IR bands of $CaTiO_3$ with the incorporation of Fe_2O_3.
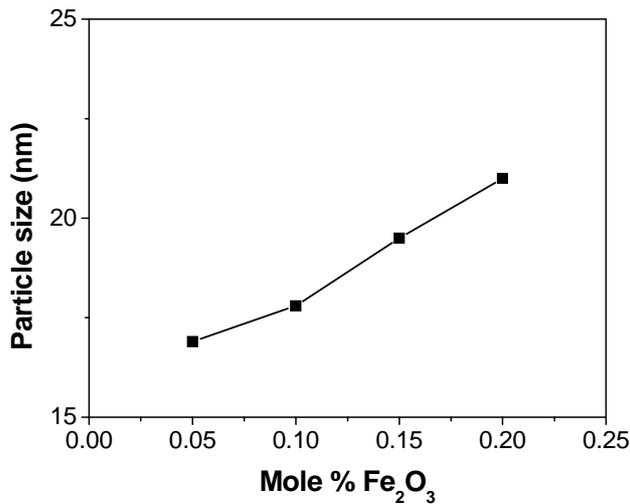
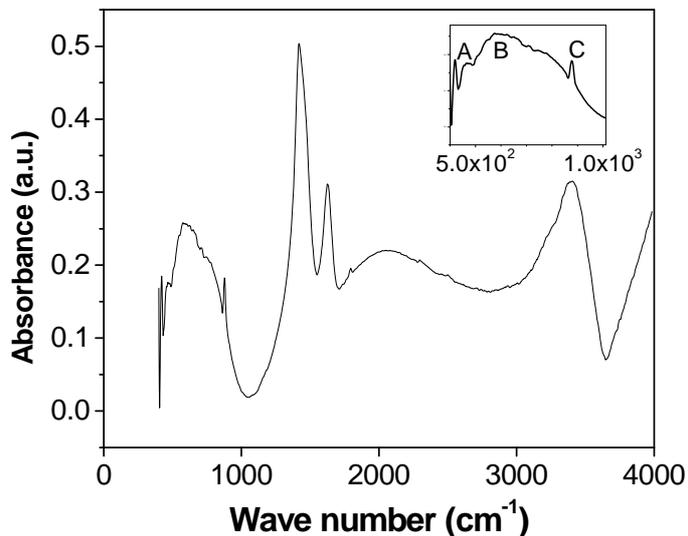**Figure 3.** Variation of particle size with doping concentration for the sample annealed at 600°C for 30 min.

Figure 4. FTIR spectrum of 0.1% Fe_2O_3 doped sample annealed at 600°C for 30 min.

The fundamental optical band gap of the samples has been computed based on their UV-absorption spectra, for understanding their optically induced transitions. There are two types of optical transitions, which can occur at the fundamental absorption edge of crystalline and noncrystalline materials. They are direct and indirect transitions. In both the cases, electromagnetic waves interact with the electrons in the valence band, which are raised across the fundamental band gap to the conduction band. For photon energies $h\nu$ just above the fundamental edge, the absorption coefficient α follows the standard relation:

$$\alpha h\nu = A(h\nu - E_g)^{1/2}$$

where A is a constant and E_g is defined as the energy band gap. A plot of $(\alpha h\nu)^2$ versus $h\nu$ for the two different annealed samples having 0.05 % and 0.15 % Fe_2O_3 respectively are presented in Fig.5. Extrapolation of this plot to $(\alpha h\nu)^2 = 0$ gives the optical band gap E_g for direct transition [15]. It is observed that the optical band gap decreases while the concentration of Fe_2O_3 increases. The estimated value of the gap varies from 4.3 to 3.7 eV while the iron concentration varies from

0.05 to 0.2 mole % and is presented in Fig. 6. The decrease of optical bandgap with the increase of Fe_2O_3 can be ascribed to the formation of impurity levels in the mid-gap region.
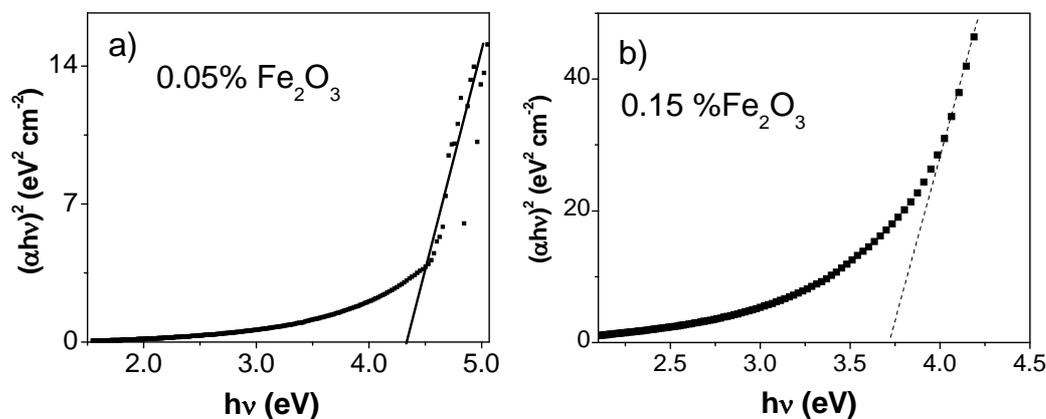

Figure 5. Plot of $(\alpha h\nu)^2$ versus $h\nu$ for the samples annealed at 600°C for 30 min.; (a) 0.05 % F_2O_3 and (b) 0.15 % F_2O_3.
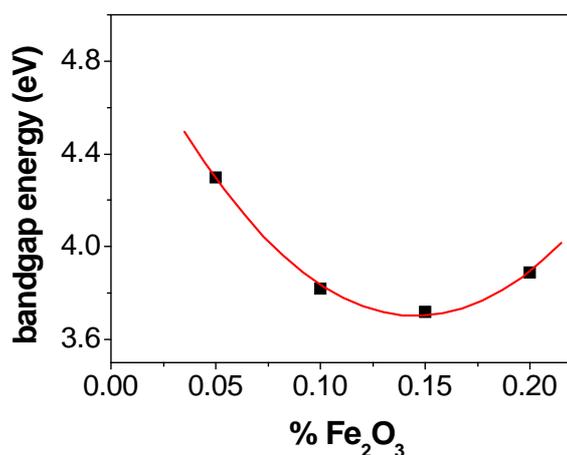

Figure 6. Variation of optical band gap with doping concentration.

Conclusions

Iron oxide doped nanocrystalline $CaTiO_3$ have been prepared using a soft chemical route, which is inexpensive and very easy. Results demonstrate that it is possible to grow single-phase ceramic $CaTiO_3$ phase within 500°C, which is quite low for the perovskite than materials prepared by conventional ceramic process. Rietveld analysis shows that size of the iron oxide doped $CaTiO_3$ is in nanocrystalline range and it increases with the increase of Fe_2O_3 content. Optical band gap decreases with increase of Fe_2O_3 doping. Effect of Fe_2O_3 doping on high temperature phase transformation study is underway.

Acknowledgements

References

[1]   (a) J. Hao, W. Si and X.X. Xi, Appl. Phys. Lett. 76(2000)3100; (b) J.P. Wiff, V.M. Fuenzalida, J.L. Arias and M.S. Fernandez, Mat. Lett. 61(2007)2739.

[2]   Y.X. Wang, W.L. Zhong, C.L. Wang and P.L. Zhang, Solid St. Commun. 117(2001)461.

[3]   H.F. Naylor and O.A. Cook, J. Am. Chem. Soc. 68(1946)1003.

[4]   T. Vogt and W.W. Schmahl, Euro phys. Lett. 24(1993)281.

[5]   X. Zhang, J. Zhang, X. Zhang, L. Chen, Y. Luo and X-J. Wang, Chem. Phys. Lett. 434(2007)237.

[6]   F.M. Figueiredo, M. R. Soares, V. V. Kharton, E. N. Naumovich, J. C. Waerenborgh and J.R. Frade, J. Electroceramics 13(2004)627.

[7]   M. Maglione and M. Belkaoumi, Phys. Rev. B 45(1992) 2029.

[8]   H. Iwahara, T. Esaka and T. Mangahara, J. Appl. Electrochem. 18(1988)173.

[9]   J-C. Grenier, G. Schiffmacher, P. Caro, M. Pouchard, P. Hagenmuller, J. Sol. St. Chem. 20 (1977)365.

[10] J.M.D. Coey, Phys. Rev. Lett. 27(1971)1140.

[11] R.W. Siegel, S. Ramasamy, H. Hahn, Z. Li, T. Lu and R. Gronsky, J. Mater. Res. 3(1989)1367; J. Non- Cryst. Solids 100 (1988)1.

[12] M. Pal, D. Das, S. N. Chintalapudi and D. Chakravorty, J. Mater. Res. 15 (2000)683.

[13] L. Lutterotti, MAUD version 1.85, (2002), http:/www.ing.unitn.it/~luttero/maud.

[14] P. Bose, S. Bid, S.K. Pradhan, M. Pal and D. Chakravorty, J. Alloy. Comp. 343 (2002) 192.

[15] L. Edwards and M. Gouterman, J. Mol. Spectr. 33(1970) 299.

Effect of Iron Substitution on Structure and Optical Properties of Nanocrystalline CaTiO₃