International Journal of Research in Advent Technology, Vol.6, No.10, October 2018
E-ISSN: 2321-9637
Available online at www.ijrat.org

Synthesis and characterization of Eu:$CaTiO_3$ nanopowder by using sol-gel method

S. Anjelin Ursula Portia[a], K. Ramamoorthy[b,*]
[a] *Research scholar of Physics, Research and Development Centre, Bharathiar University, Coimbatore– 641046, India*
[b] *Assistant professor of Physics, Govt. Arts & science College, Komarapalayam - 638183, India.*
E.mail: anjelin1980@gmail.com[a]

Abstract- The main work is to synthesize perovskite type of Eu doped $CaTiO_3$ nanopowder using sol-gel method. The as-synthesized sample was characterized by various highly developed techniques. The Structural analysis was calculated by using X-ray Diffraction Method (XRD). The functional groups were examined by using Fourier Transform Infrared Spectrophotometer (FTIR). The Surface structure was examined by Scanning Electron Microscopy (SEM). The elemental configuration was calculated by Energy Dispersive X-Ray Spectroscopy (EDAX) . The optical property was obtained by Ultra - Violet visible Infrared Spectroscopy (UV-vis DRS), and the Microstructure analysis were performed by using high resolution transmission electron spectroscopy (HRTEM). This technique is suitable, low price, simple, and successful in comparison to the familiar methods of the synthesis of nanopowders.

Key words: nanopowder;, Eu:$CaTiO_3$; sol-gel

1. INTRODUCTION

TiO_2 has a broad variety of applications. They are UV filters for optics and packing equipment [1], humidity sensors [2], antireflection coatings for photovoltaic cells and passive solar collectors [3], transparent conductors [4], electro chromic displays [5], photo catalysts for refinement and treatment of water and air [6], gas sensors [7], anodes for lithium-ion batteries [8], and self cleaning coatings of windows and tiles [9], These oxides have some characteristics such as pyroelectrical, dielectrical, ferroelectric, photo restrictive, piezoelectric, magneto restrictive, and electro-optical characters [10, 11].

$CaTiO_3$, being one of the member of perovskite Family. It has many usage such as dielectric resonators in wireless communication system [12], bio-medical, [13], equipment operating at microwave frequencies [14], photo catalytic [15] . Calcium Titanate doped with rare earth ions grant a variety of applications in the fields of opto-electronic devices [16-19].It has lot of attraction among the researchers because of their friendly environment ,luminescence properties and well- known chemical stability . They are used in field emission displays and white light emitting diode devices[19].

Number of methods have been suggested in literature for synthesizing Eu:$CaTiO_3$ powders. This type of perovskite was initially equipped by solid state reaction at room temperatures 1623k [20]. In this method we perceive a number of problem, such as in-homogeneity, high –processing temperatures and infectivity by impurities with a non uniform particle sizes allocation [21]. These troubles can be condensed by wet chemical methods. So wet chemical methods have been employed to synthesize $CaTiO_3$ powders, such as a hydrothermal process[22], sol-gel[23], co-precipitation [24],organic-inorganic solution technique[25] and combustion method[26].The optical performance depends preparation method, structural organization and heat behavior conditions[27].

Sol-gel procedure is a positive method that offers relative low price, uniform, and high clarity of the ceramics. In the present study, we have reported about the Eu:$CaTiO_3$ nanopowder synthesized by using sol-gel technique. The sample was analyzed by using XRD, FTIR, SEM , EDAX, UV and HRTEM

2. EXPERIMENTAL SECTION

2.1 Materials used

The chemicals used in this synthesis were Calcium chloride ($CaCl_2$) as a resource for calcium, Titanium (IV) isopropoxide ($Ti(OC_4H_9)_4$) as a resource for titanium , Europium di-oxide (Eu_2O_3) as a resource for europium, citric acid ,ethanol , HNO_3 and ultra pure water were the solvents.

2.2 Sample preparation

The sample were synthesized by using sol-gel method. For this synthesis a solution of Ca: Ti: Citric acid: ethanol mole ratio 0.8: 1: 1:1 was magnetic stirred for an hour. After that 0.2 mole of Eu_2O_3 solution was prepared by adding Eu_2O_3 to a 10:1 mixture of ethanol and HNO_3 and stirred for 1 hour. Then both the solutions were added and allowed to stir and evaporated at 70°C for 2 hours. Then it was dried in a hot plate for overnight and the solvent was removed by heating to at 100°C. The resulting powder was annealed at different temperatures like 500°C , 700°C and 900°C for 2 hours in a muffle furnace. Then the as-synthesized samples were crushed in to powder to form Eu:$CaTiO_3$ nanopowder.

2.3 Characterization of Eu : $CaTiO_3$ nanopowder

The as-synthesized Eu : $CaTiO_3$ samples were characterized by various superior techniques. The Structural analysis were monitored by X-ray Diffractometry (XRD) in the 2Θ range from 5° to 90° .The FTIR micro-analysis were carried out and it covers the range of wavenumbers from 400 to 4000 cm^{-1}. The Surface Morphology were measured using Scanning Electron Microscopy (SEM). The Composition was studied using Energy Dispersive X-Ray Spectroscopy(EDAX), The Optical band gap was recorded using Ultra - Violet visible Infrared Spectroscopy (UV-Vis) from 200-900 nm, and the Microstructure investigation were analyzed by using High Resolution Transmission Electron Spectroscopy(HRTEM).

3. RESULTS AND DISCUSSIONS

3.1 X-ray diffraction analysis

The structure and crystallite size was investigated by X-ray diffraction (XRD) using Bruker diffractometer within the 2θ range of 5° to 90° using CuKα as X-ray source **(λ=1.5406Å).** The following calculations were done.The particle size of the nanopowder was calculated based on Scherer's equation [28], the Scherrer's equation is described as

$$\mathbf{D} = \frac{\mathbf{K\lambda}}{\boldsymbol{\beta}\mathbf{COS\theta}} \text{ (nm)} \text{ ---------Eq.(1)}$$

Where, D : mean crystallite size, K : shape factor taken as 0.94, λ : wavelength of the incident beam, β : full width at half maximum and θ : Bragg angle. The Dislocation density is calculated by:

$$\boldsymbol{\delta} = \frac{\mathbf{1}}{\mathbf{D^2}} \text{ lines/m}^2 \text{ ---------Eq.(2)}$$

The strain is calculated by using the equation:

$$\boldsymbol{\eta} = \frac{\boldsymbol{\beta}\, cos\theta}{\mathbf{4}} \text{ ---------Eq.(3)}$$

The Micro strain is calculated by using the equation:

$$\boldsymbol{s} = \frac{\boldsymbol{d}}{\boldsymbol{D\sqrt{12}}} \text{ ---------Eq.(4)}$$

Parameters	**700** °C	**900** °C
Max peak (2θ)	33.31	33.15
FWHM (β) (degree)	0.269	0.2297
Interplanar spacing (d) (Å)	2.7563	2.7693
Particle size (D) (nm)	31.634	37.0469
Strain η	1.1737 E-3	1.0022 E-3
Dislocation density (ρ) l/m²	0.9992 E+15	0.7286 E+15
Micro strain (s)	2.5152 E-3	2.15788 E-3

Table 1: Parameters of Eu doped $CaTiO_3$ nanopowder in a sol-gel method

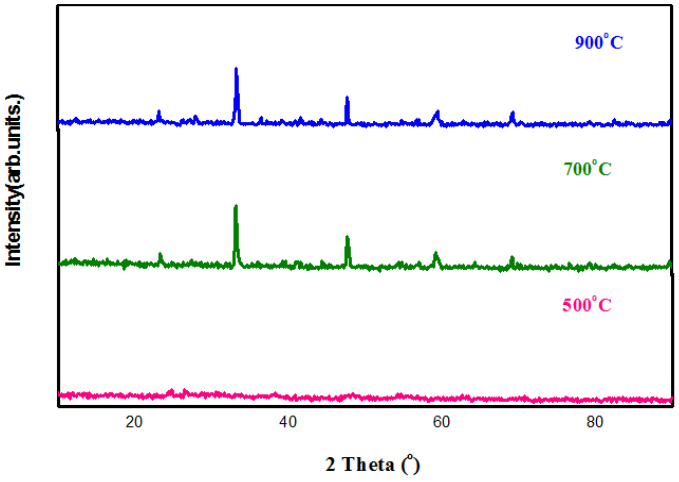

Fig.1. XRD pattern of Eu:$CaTiO_3$ nanopowder annealed at different temperature

The increase of temperature leads to the $CaTiO_3$ phase. Comparing the annealing temperature, at 900°C the sample displayed a superior crystallization. Above 1580 °C the formation of $CaTiO_3$ is Cubic ,amid 1500 °C to 1580 °C it is tetragonal, below 1500 °C it is orthorhombic[29,30]. All the peaks can be assigned to the orthorhombic

organization is shown in fig.1 . Increase of temperature cause an increase in the particle size is shown in fig.2. This performance can be linked with the aggregates making and nuclei formation [31] . $CaTiO_3$ phase was conformed by the comparison between the XRD patterns with the JCPDS card no. 88-0790.

Lattice parameters	JCPDS (88-0790)	700°C	900 °C
a (Å)	5.378	5.5126	5.5380
b(Å)	5.444	5.6105	5.50412
c(Å)	7.637	7.8213	7.8244

Table 2: Lattice Parameters of Eu:$CaTiO_3$ nanopowder synthesized by sol-gel method.

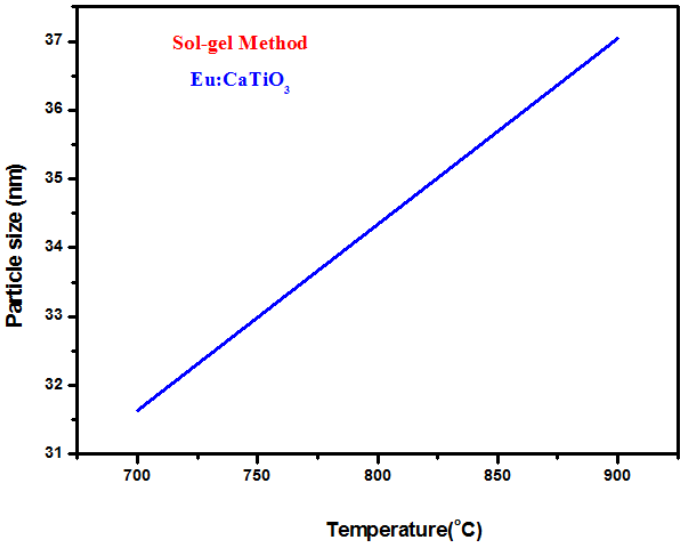

Fig.2.Particle sizes as a function of heat treatment of Eu:$CaTiO_3$ nanopowder synthesized by sol-gel method

3.2 FTIR Analysis

FTIR analysis were performed for the powder sample annealing temperature at 900 °C . Fig.3 shows the FTIR spectra of Eu:$CaTiO_3$ nanopowder prepared by sol-gel method.Table 3 gives the FTIR analysis of Eu :$CaTiO_3$ nanopowder. The band at 3377.26cm^{-1} was related to the super position of the vibration band of the hydroxyl group and the stretching vibration of the adsorbed water molecule. The C-H stretching band is occurred at 2924.78cm^{-1} . The COOH stretching band is occurred at 2856.07cm^{-1} . The C ≡ C stretching band is occurred at 2264.99cm^{-1} The band at 1633.23 cm^{-1} are due to symmetric stretching vibrational modes of metal-oxygen bond. The C-H bending band is occurred at 1384.79cm^{-1} The C-O stretching band is occurred at 1118.59cm^{-1} and 1066.88 cm^{-1} .A band around 571.90cm^{-1} and 430.24cm^{-1} are caused by stretching vibration due to interactions produced between the oxygen and the metal bonds..

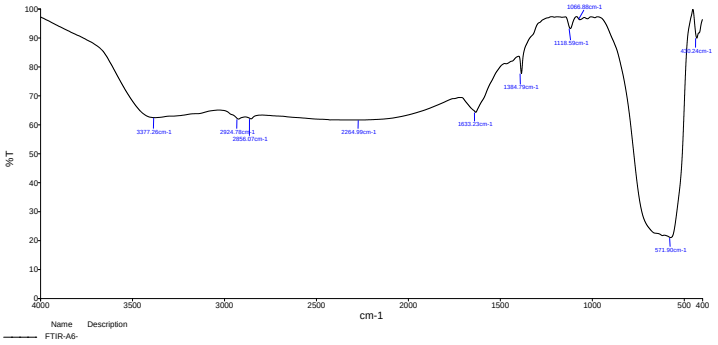

Fig.3 . FTIR spectra of Eu : $CaTiO_3$ nanopowder prepared by sol-gel method

Wave number cm^{-1}	Functional group	Types of vibrations	Intensity	Class of Compounds
3377.26	O-H	Stretching, H-bonded	Strong, Broad	Alcohols
2924.78	C-H	Stretching	Strong	Alkane
2856.07	COOH	Stretching	Strong	Enols
2264.99	C ≡ C	Stretching	Variable	Alkynes
1633.23	C=C	Stretching	Variable	Alkenes
1384.79	C-H	Bending	Strong	Methyl groups
1118.59	C-O	Stretching	Strong	Carbonyl groups
1066.88	C-O	Stretching	Strong	Carbonyl groups
571.90	C-Cl	Stretching	Strong	Alkyl Halide
430.24	C-Cl	Stretching	Strong	Alkyl Halide

Table 3 FTIR analysis of Eu :$CaTiO_3$ nanopowder prepared by sol-gel method

3.3 Surface morphology analysis

Fig.4 shows the SEM analysis of Eu : $CaTiO_3$ nanopowder synthesized by sol-gel method. The product show foamy and porous with agglomerated particles. The particles are nearly spherical in shape.

The introduction of Eu ions does not change the $CaTiO_3$ morphology.

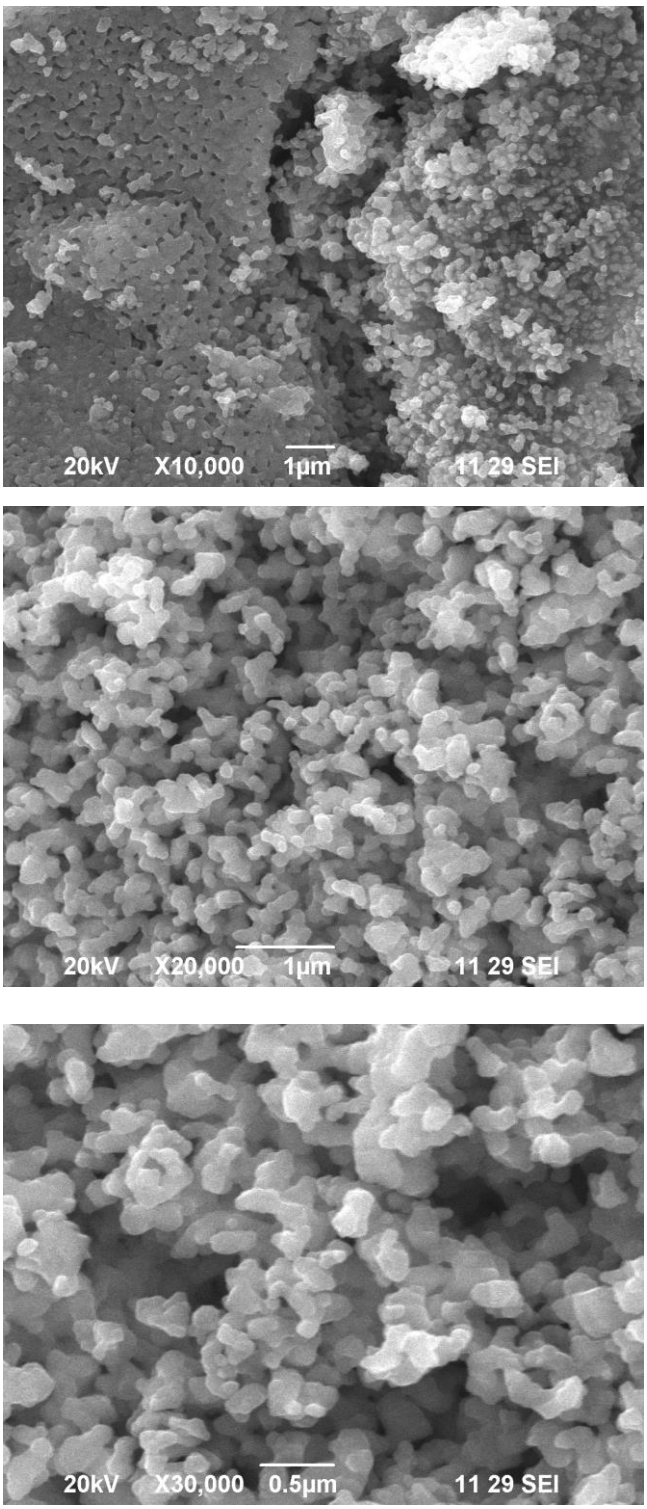

Fig.4 .SEM analysis of Eu :$CaTiO_3$ nanopowder prepared by sol-gel method

3.4 Energy dispersive x-ray spectroscopy analysis

The EDAX measurement of the Eu : $CaTiO_3$ nanopowder prepared by sol-gel method is shown in Fig.5. The EDAX examination indicated that the nanostructures are composed of Ca, Ti, Eu and O atoms and it exhibits clear peaks of only Ca, Ti, Eu and O elements, whereas no additional peaks were established, which means that the Eu :$CaTiO_3$ powder is exempted from impurities.

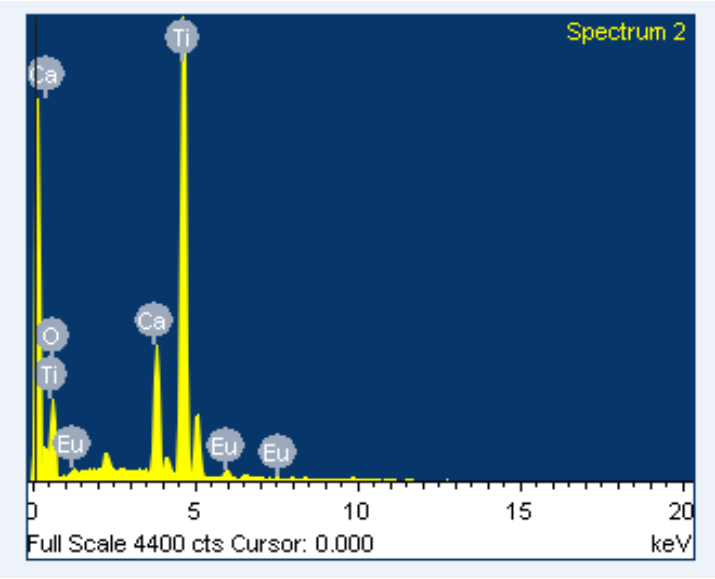

Fig .5. EDAX analysis of Eu :$CaTiO_3$ nanopowder prepared by sol-gel method

Table 4 shows that the atomic and weight percentage of Eu doped $CaTiO_3$ powder prepared by sol-gel method.

Table 4 : EDAX analysis of Eu : $CaTiO_3$ nanopowder prepared by sol-gel method

Element	Series	Weight %	Atomic %
O	K	44.17	70.47
Ca	K	17.97	13.07
Ti	K	35.02	15.98
Eu	L	2.84	0.48

3.5 Ultra - violet visible infrared spectroscopy analysis

The optical properties of Eu:$CaTiO_3$ nanopowder prepared by sol-gel method was analyzed by UV-VIS diffusion reflectance spectroscopy in the wavelength range of **200 – 900 nm.**

UV absorption spectra of Eu :$CaTiO_3$ nanopowder was obtained from the diffuse reflectance data by using the Kubelka-Munk function[32]. The optical band gap energy was 2.99ev corresponds to optical absorption edge of 381 nm . Fig .6. shows the Optical band gap calculation of Eu:$CaTiO_3$ nanopowder

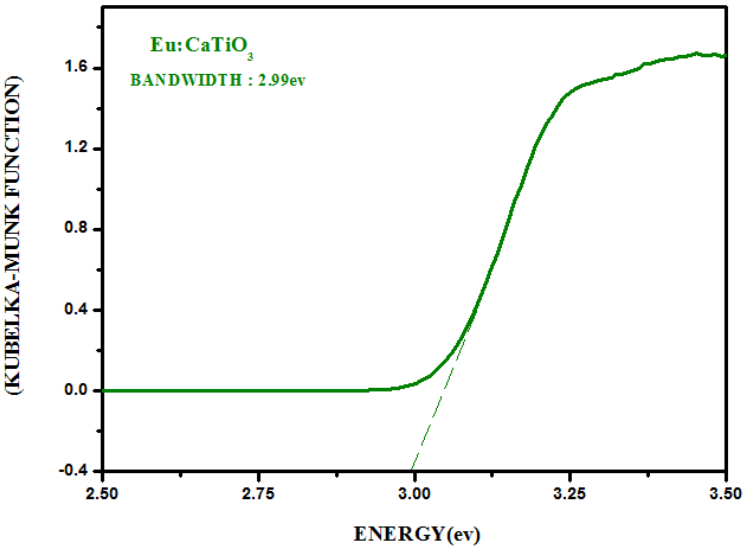

Fig .6. Optical band gap calculation of Eu :$CaTiO_3$ nanopowder prepared by sol-gel method

3.6 High resolution transmission electron microscopy

The microstructure of Eu :$CaTiO_3$ nanopowder prepared by sol-gel method was examined by HRTEM. Fig 7a is the high –resolution image of Eu :$CaTiO_3$ nanopowder which exhibits the clear lattice fringes. The interlayer spacing 0.15nm is corresponds to (204) plane of $CaTiO_3$.

Fig.7b shows the selected area electron diffraction (SAED) pattern of Eu :$CaTiO_3$ nanopowder calcined at 900^{o}C. The circular bright continuous rings in the SAED pattern reveals the fact that particles where nanosized and confirmed the crystalline nature of nanopowder. Fig.7c shows the grains of the of Eu :$CaTiO_3$ nanopowder look like sphere.

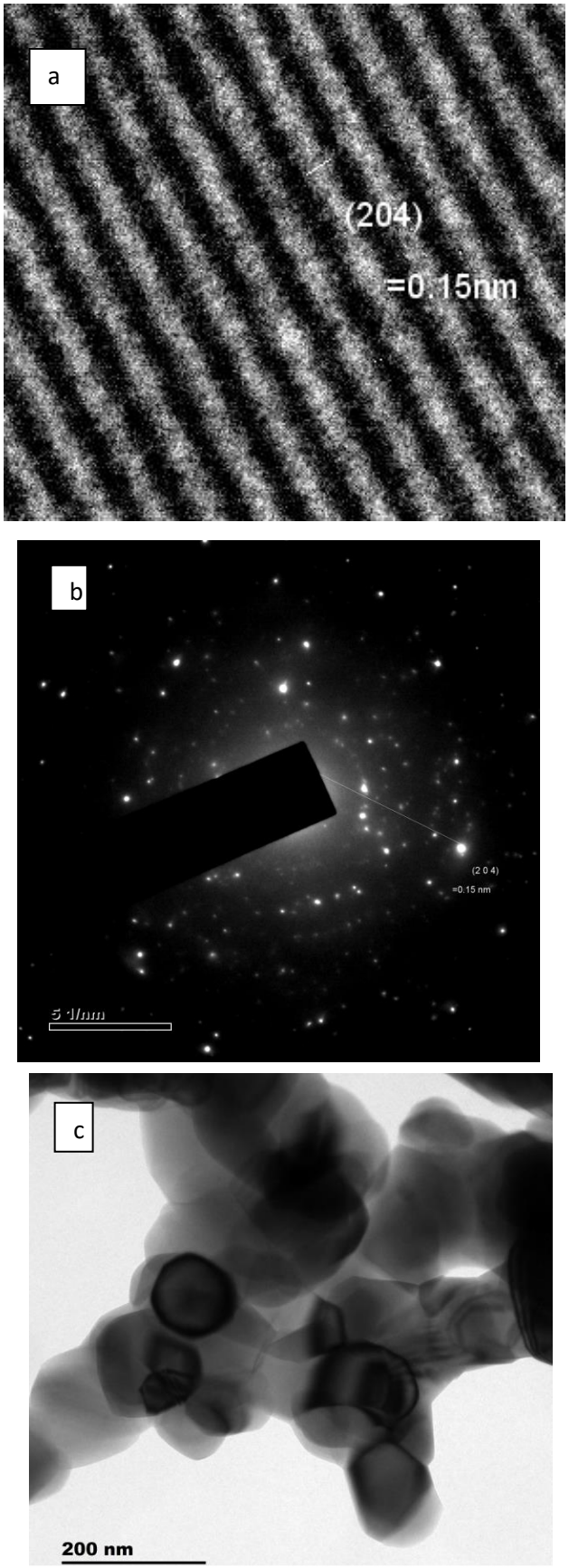

Fig . 7 a,b.c: HRTEM micrographs of Eu:$CaTiO_3$ nanopowder prepared by sol-gel method calcined at 900°C

4. CONCLUSION:

Eu:$CaTiO_3$ nanopowder prepared by using sol-gel method at low temperature calcinations . The sample was characterized by various advanced techniques. Particles were sphere-shaped and the Particle size was from 31-37nm, and the lattice parameters are a=5.523(Å), b=5.607(Å), c=7.8013(Å). The band width is 2.99ev. The interlayer spacing 0.15nm is corresponds to (204) plane of $CaTiO_3$. The functional group, surface morphology and compositional analysis were carried out using FTIR,SEM and EDAX respectively.

REFERENCE

[1] Ivanova T, Harizanova A, Surtchev M, Nenova Z (2003) Investigation of sol–gel derived thin films of titanium dioxide doped with vanadium oxide. Sol Energy Mater Sol Cells 76:591–598.

[2] Su PG, Huang LN (2007) Humidity sensors based on TiO2 nanoparticles/polypyrrole composite thin films. Sens Actuators B Chem 123:501–507

[3] Shan MN, Wang SS, Bian ZQ, Liu JP, Zhao JL (2009) Hybrid inverted organic photovoltaic cells based on nanoporous TiO2 films and organic small molecules. Sol Energy Mater Sol Cells 93:1613–1617.

[4] Lansaker PC, Backholm J, Niklasson GA, Granqvist CG (2009) TiO2/Au/TiO2 multilayer thin films: novel metal-based transparent conductors for electrochromic devices. Thin Solid Films 518:1225–1229.

[5] Toma SH, Toma HE (2006) Versatile electrochromic displays based on TiO2 nanoporous films modified with triruthenium clusters. Electrochem Commun 8:1628–1632

[6] Ao CH, Lee SC (2005) Indoor air purification by photocatalyst TiO2 immobilized on an activated carbon filter installed in an air cleaner. Chem Eng Sci 60:103–109

[7] Mohammadi MR, Fray DJ (2007) , Semiconductor TiO2–Ga2O3 thin film gas sensors derived from particulate sol–gel route. Acta Mater 55:4455–4466

[8] He BH, Dong B, Li HL (2007) Preparation and electrochemical properties of Ag-modified TiO2 nanotube anode material for lithium–ion battery. Electrochem Commun 9:425–430

[9] Yuranova T, Mosteo R, Bandara J, Laub D, Kiwi J (2006) Selfcleaning cotton textiles surfaces modified by photoactive SiO2/TiO2 coating. J Mol Catal A Chem 244:160–167

[10] Montenero A, Canali M, Gnappi G, Bersani D, Lottici PP,Nunziante P, Traversa E (1997) Structural and electrical properties of sol-gel processed CdTiO3 powders and films. Appl Organomet Chem 11:137–146

[11] . Zhang X, Wang H, Huang A, Xu H, Zhang Y, Yu D, Wang B,Yan H (2003) Synthesis of cadmium titanate powders by a solgel-hydrothermal method. J Mater Sci 38:2353–2356

[12] S.Y. Lee, M.C.C. Custodio, H.J. Lim, R.S. Feigelson, J.P. Maria, S. Trolier- McKinstry, J. Cryst. Growth 226 (2001) 247.

[13] Stanishevsky AV, Holliday S (2007) Mechanical properties of sol–gel calcium titanate bioceramic coatings on titanium. Surf Coat Technol 202:1236–1241

[14] Kim JS, Cheon CI, Kang HJ, Lee CH, Kim KY, Nam S, Byun JD (1999) Crystal structure and microwave dielectric properties of CaTiO3–(Li1/2Nd1/2)TiO3–(Ln1/3Nd1/3)TiO3 (Ln = La, Dy) ceramics. Jpn J Appl Phys 38:5633–5637

[15] Zhang D, Zhang CL, Zhou P (2011) Preparation of porous nano calcium titanate microspheres and its adsorption behavior for heavy metal ion in water. J Hazard Mater 186:971–977

[16] P. Boutinaud, E. Tomasella, A. Ennajdaoui, R. Mahiou, Structural characterization and luminescent properties of CaTiO3:Pr3þ thin films deposited by radio frequency sputtering, Thin Solid Films 515 (2006) 2316-2321

[17] A.T. de Figueiredo, V.M. Longo, S. de Lazaro, V.R. Mastelaro, F.S. De Vicente, A.C. Hernandes, et al., Blue-green and red photoluminescence in CaTiO3:Sm, J. Lumin 126 (2007) 403-407.

[18] P.J. Dere_n, R. Mahiou, R. Pa¸ zik, K. Lemanski, W. Stre¸ k, P. Boutinaud, Upconversion emission in CaTiO3:Er3þ nanocrystals, J. Lumin 128 (2008) 797-799.

[19] B. Marí, K.C. Singh, P. Cembrero-Coca, I. Singh, D. Singh, S. Chand, Red emitting MTiO3 (M ¼ Ca or Sr) phosphors doped with Eu3þ or Pr3þ with some cations as co-dopants, Displays 34 (2013) 346-351.

[20] H.F. Kay, P.C. Bailey, Structure and properties of CaTiO3, Acta Cryst. 10 (1957) 219–226.

[21] I.R. Evans, J.A.K. Howard, T. Sreckovic, M.M. Ristic, Variable temperature in situ X-ray diffraction study of mechanically activated synthesis of calcium titanate, CaTiO3, Mater. Res. Bull. 38 (2003) 1203–1213.

[22] T.R.N. Kutty, R. Vivekanandan, P. Murugaraj, Precipitation of rutile and anatase (TiO2) fine powders and their conversion to MTiO3 (M= Ba, Sr, Ca) by the hydrothermal method, Mater. Chem. Phys. 19 (1988) 533–546.

[23] G. Pfaff, Synthesis of calcium titanate powders by the sol–gel process, Chem. Mater. 6 (1994) 58–62.

[24] X. Zhang, J. Zhang, X. Ren, X.-J. Wang, The dependence of persistent phosphorescence on annealing temperatures in CaTiO3:Pr3+ nanoparticles prepared by a coprecipitation technique, J. Solid State Chem. 181 (2008) 393–398.

[25] S.J. Lee, Y.C. Kim, J.H.Hwang, An organic–inorganic solution technique for fabrication of nano-sized CaTiO3 powder, J. Ceram. Process. Res. 5 (2004) 223–226.

[26] M. Muthuraman, K.C. Patil, S. Senbagaraman, A.M. Umarji, Sintering, microstructural and dilatometric studies of combustion synthesized synroc phases, Mater. Res. Bull. 31 (1996) 1375–1381.

[27] L.S. Cavalcante, M.F.C. Gurgel, E.C. Paris, A.Z. Sim˜oes, M.R. Joya, J.A. Varela, P.S.Pizani, E. Longo, Combined experimental and theoretical investigations of the photoluminescent behavior of Ba(Ti, Zr)O3 thin films, Acta Mater. 55 (2007) 6416–6426.

[28] C. Suryanarayana, M.G.Norton, X-Ray Diffraction: A Practical Approach, Plenum Press, New York, 1998.

[29] Jianhua Hao, Weidong Si, X. X. Xi, Ruyan Guo, AS. Bhalla, LB. Cross, Applied Physics Letters, 76 (21), 3100(2000).

[30] H. Veenhuis, T. Borger, K. Peithmann, M. Flaspohler, K. Buse, R. Pankrath, H.Hesse, E. Kratzig, Appl. Phys. B 70,797 (2000)

[31] G. Zhou, M. L ¨ u, F. Gu, D. Xu, D. Yuan, J. Cryst. Growth 276 (2005) 577–582

[32] Phosphor Handbook edited under the Auspices of Phospor Research Society,editorial committee co-chairs: Shigeo Shionoya, William M. Yen, CRC Press, Boca Raton Boston London, Newyork, Washington DC, 1999, p. 763.