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Preparation and Characterization of $CaTiO_3$ Nanopowder by Using Sol-gel Method

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Abstract

The aim is to prepare perovskite type of $CaTiO_3$ nanopowder using sol-gel method. The prepared samples were characterized by different highly developed techniques. The Structural investigation of nanopowder was investigated by using X-ray Diffraction Method (XRD). The Functional groups were analyzed by using Fourier Transform Infrared Spectrophotometer (FTIR). The Surface Morphology was analyzed by using Scanning Electron Microscopy (SEM). The elemental Composition was deliberate by using Energy Dispersive X-Ray Spectroscopy (EDAX) . The bandwidth was obtained by Ultra - Violet visible Infrared Spectroscopy (UV-vis DRS), and the Microstructure investigation were performed by using high resolution transmission electron spectroscopy (HRTEM). This method is convenient, low cost, easy, simple, and effective in evaluation to the known methods of the synthesis of nanopowders.

Key words: *$CaTiO_3$, nanopowder, sol-gel.*

1. Introduction

Titanium Dioxide has a broad range of applications, such as ultraviolet filters for optics and packing materials [1], transparent conductors [2], antireflection coatings for photovoltaic cells and passive solar collectors [3], humidity sensors [4], electro chromic displays [5], anodes for lithium-ion batteries [6], gas sensors [7], photo catalysts for purification and treatment of water and air [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].

Calcium Titanate, being one of the member of this Family. It can be in different applications such as dielectric resonators in wireless communication system [12], biomedical, [13], photo catalytic [14] and communication equipment operating at microwave frequencies [15]. It has assortment of attraction amongst the researchers because of their friendly environment, luminescence properties and well- known chemical stability.

Many methods have been reported in literature for preparing $CaTiO_3$ nanopowders. This type of perovskite was firstly prepared by conventional solid state reaction at room temperatures 1623k [16]. In this method we observed a numeral of problem, such as in-homogeneity, high –processing temperatures and contamination by impurities with a non uniform particle sizes distribution[17]. These problems can be abridged by wet chemical methods. So wet chemical methods have been employed for the preparation of $CaTiO_3$ nanopowders, such as co-precipitation [18], hydrothermal process[19], combustion method[20], organic-inorganic solution technique[21] and sol-gel[22]. The optical behavior depends preparation method, structural organization and heat treatment conditions [23].

Sol-gel method is a hopeful method that offers relative low price tag, harmonized, identical size, and high transparency of the ceramics. In this study, we have reported about the $CaTiO_3$ nanopowder prepared by using sol-gel technique. The powder sample was characterized by using XRD, FTIR, SEM , EDAX, UV and HRTEM

2. Experimental Section

2.1 Materials Used

The chemicals used in this preparation were Calcium chloride ($CaCl_2$) as a source for calcium, Titanium (IV) isopropoxide ($Ti(OC_4H_9)_4$) as a source for titanium , citric acid ,ethanol and ultra

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pure water were the solvents. All reagents were used as received without any further refinement.

2.2 Sample Preparation

The nanopowder was prepared by using sol-gel method. For this synthesis a solution of Ca: Ti: Citric acid: ethanol mole ratio 1: 1: 1:1 was magnetic stirred and evaporated at 70°C for 2 hours. Then it was dried out 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. The annealed samples were crushed in a mortar to form $CaTiO_3$ nanopowder.

2.3 Characterization of Eu : $CaTiO_3$ Nanopowder

The annealed $CaTiO_3$ samples were characterized by different advanced techniques. The Structural analysis was 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 wave numbers from 400 to 4000 cm^{-1}. The Surface Morphology were measured using Scanning Electron Microscopy (SEM). The elemental composition was studied using Energy Dispersive X-Ray Spectroscopy(EDAX), The Optical band gap was recorded by using Ultra - Violet visible Infrared Spectroscopy (UV-vis DRS), and the Microstructure analysis was investigated by using High Resolution Transmission Electron Spectroscopy(HRTEM).

3. Results and Discussions

3.1 X-Ray Diffraction Analysis

The structure and crystallite size was analyzed 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 formulas were used in the calculations:

The crystallite size of the nanopowder was calculated based on Scherer's equation as reported in the literature[24], the Scherrer's equation is described as follows:

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

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.

$$\mathbf{2d_{hkl}\ sin\ (\theta) = n\lambda} \quad \text{------ Eq. (2)}$$

Where, d is the spacing between the planes in the atomic lattice. h, k, and l are all integers, (hkl) is the lattice plane index, a, b and c are lattice constants, d_{hkl} is the distance between two consecutive planes (n=1) with plane index (hkl).
The Dislocation density is calculated by:

$$\boldsymbol{\delta} = \frac{\mathbf{1}}{\mathbf{D^2}} \text{ lines/m}^2 \quad \text{------ Eq. (3)}$$

The Micro strain is calculated by using the equation:

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

The strain is calculated by using the equation:

$$\boldsymbol{\eta} = \frac{\boldsymbol{\beta}\ \boldsymbol{cos}\theta}{\mathbf{4}} \quad \text{------ Eq. (5)}$$

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

S.No	Parameters	700°C	900°C
1	Max peak (2θ)	33.19	33.29
2	FWHM (β) (degree)	0.31725	0.26981
3	Interplanar spacing (d) (Å)	2.766	2.7579
4	Particle size (D) (nm)	26.823	31.539
5	Strain $\boldsymbol{\eta}$	1.38E-03	1.18E-03
6	Dislocation density (ρ) l/m^2	1.39E+15	1.01E+15
7	Micro strain (s)	2.98E-03	2.52E-03

The increasing the temperature leads to the formation of $CaTiO_3$ phase. Comparing the annealing temperature, at 900°C the sample displayed a good crystallization. Above 1580 °C the structure of $CaTiO_3$ is Cubic ,between 1500 °C to 1580 °C it is tetragonal, below 1500 °C it is orthorhombic[29,30]. All the diffraction peaks can be assigned to the orthorhombic structure is shown in fig.1

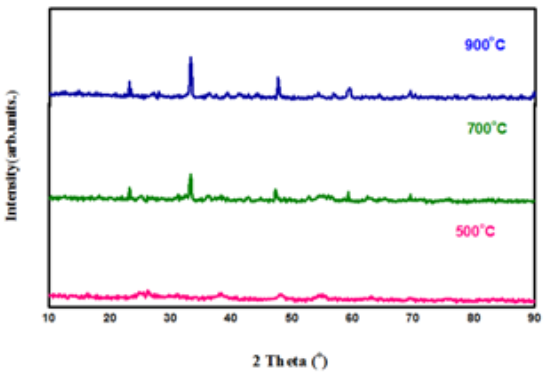

Fig.1. XRD pattern of $CaTiO_3$ nanopowder annealed at different temperature in Sol-gel method

Raise of temperature cause an increase in the crystallite size is shown in fig.2. This behavior

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can be associated with the aggregates production and nuclei formation[31]. $CaTiO_3$ phase was conformed by the assessment between the XRD patterns with the JCPDS card no. 88-0790. Table 2. Shows Lattice Parameters of $CaTiO_3$ nanopowder prepared by sol-gel method.

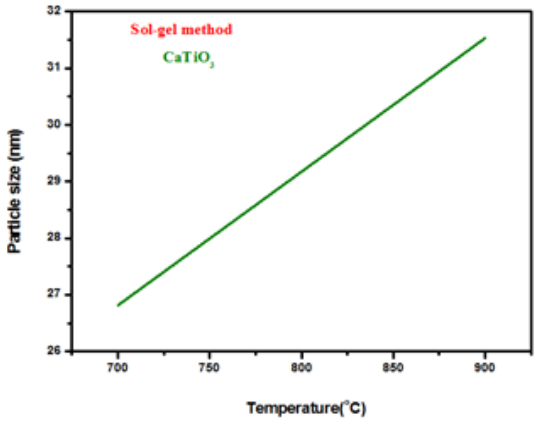

Fig 2. Particle sizes as a function of heat treatment of $CaTiO_3$ nanopowder in sol-gel method

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

S.No	Lattice parameters	JCPDS (88-0790)	700°C	900°C
.	a (Å)	5.378	5.389	5.5159
.	b(Å)	5.444	5.6531	5.4929
.	c(Å)	7.637	7.9026	7.8018

3.2 FTIR Analysis

FTIR examination was performed for the sample annealing temperature at 900°C. Fig.3 shows the FTIR spectra of $CaTiO_3$ nanopowder prepared by sol-gel technique

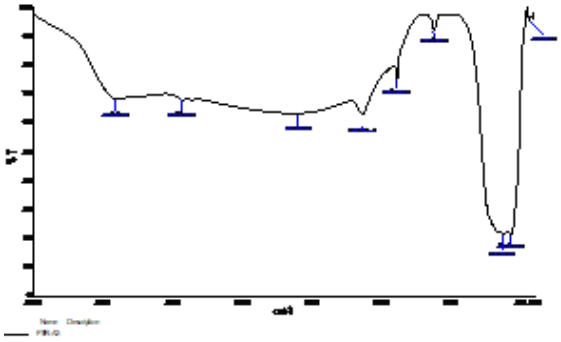

Fig.3 . FTIR spectra of $CaTiO_3$ nanopowder prepared by sol-gel technique

Table 3 gives the FTIR analysis of $CaTiO_3$ nanopowder. The band at 3395.85 cm^{-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 2925.74 cm^{-1} . C ≡ N stretching Alphatic nitriles is occurred in 2086.28. The band at 1632.75 cm^{-1} is due to symmetric stretching vibrational modes of metal-oxygen bond. The C-H bending bond is occurred at 1385.09 cm^{-1} . The C-O stretching bond is occurred 1118.78cm^{-1}. A band around 619.28 cm^{-1}, 564.51cm^{-1} and 436.89cm^{-1} are caused by stretching vibration due to interactions produced between the oxygen and the metal bonds..

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

S.No	Wave number cm^{-1}	Functional group	Types of vibrations	Intensity	Class of Compounds
1	3395.85	O-H	Stretching, H-bonded	Strong, Broad	Alcohols
2	2925.74	C-H	Stretching	Strong	Alkane
3	2086.28	C ≡ N	Stretching	Strong	Alphatic nitriles
4	1632.75	C=C	Stretching	Variable	Alkenes
5	1385.09	C-H	Bending	Strong	Methyl groups
6	1118.78	C-O	Stretching	Strong	Carbonyl groups
7	619.28	C-Cl	Stretching	Strong	Alkyl Halide
8	564.51	C-Cl	Stretching	Strong	Alkyl Halide
9	436.89	C-Cl	Stretching	Strong	Alkyl Halide

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3.3 Surface Morphology Analysis

Fig.4 shows the SEM analysis of $CaTiO_3$ nanopowder prepared by sol-gel method.

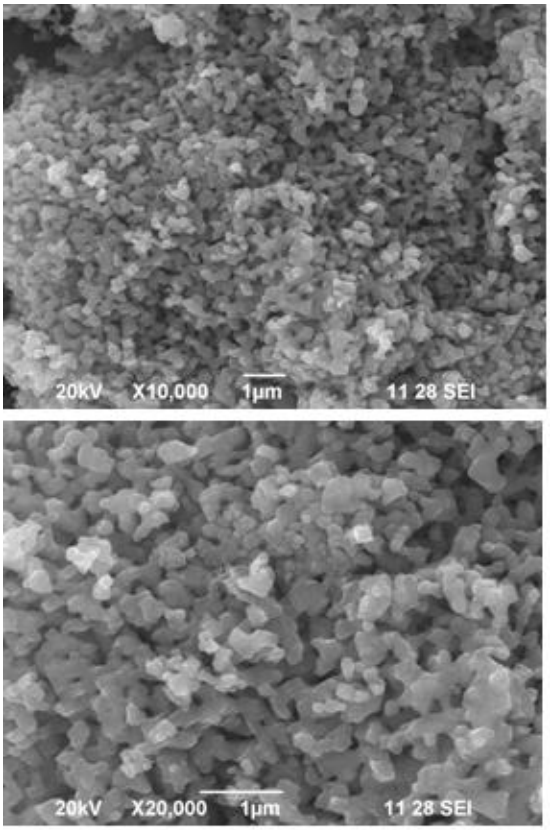

Fig.4 .SEM analysis of $CaTiO_3$ nanopowder prepared by sol-gel method

From the above figures we can conclude that the product show foamy .The particles are nearly spherical in shape.

3.4 Energy Dispersive X-Ray Spectroscopy Analysis

The EDAX measurement of the $CaTiO_3$ nanopowder is shown in Fig.5. The EDAX analysis indicated that the nanostructures are composed of Ca, Ti, and O atoms and it exhibits clear peaks of only Ca, Ti, and O elements, whereas no extra peaks were detected, which means that the $CaTiO_3$ powder is exempted from impurities.

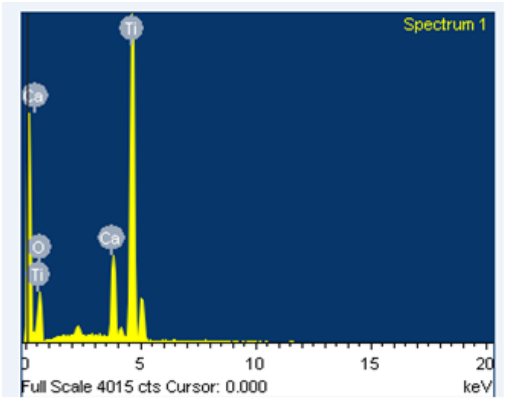

Fig .5. EDAX analysis of $CaTiO_3$ nanopowder prepared by sol-gel method

Table 4 shows that the atomic and weight percentage of $CaTiO_3$ powder

Table 4 : EDAX analysis of $CaTiO_3$ nanopowder

S.No	Element	Series	Weight %	Atomic %
1	O	K	44.30	69.87
2	Ca	K	22.68	14.83
3	Ti	K	28.02	15.30

3.5 Ultra - Violet Visible Infrared Spectroscopy Analysis

The optical properties of $CaTiO_3$ nanopowder was analyzed by UV-VIS diffusion reflectance spectroscopy using CARY 5E UV-VIS-NIR spectrophotometer (wavelength :**200 – 900 nm).** UV absorption spectra of $CaTiO_3$ nanopowder was obtained from the diffuse reflectance data by using the Kubelka-Munk function[32]. The optical band gap energy was 3.0ev corresponds to optical absorption edge of 380 nm . Fig .6. shows the Optical band gap calculation of $CaTiO_3$ nanopowder

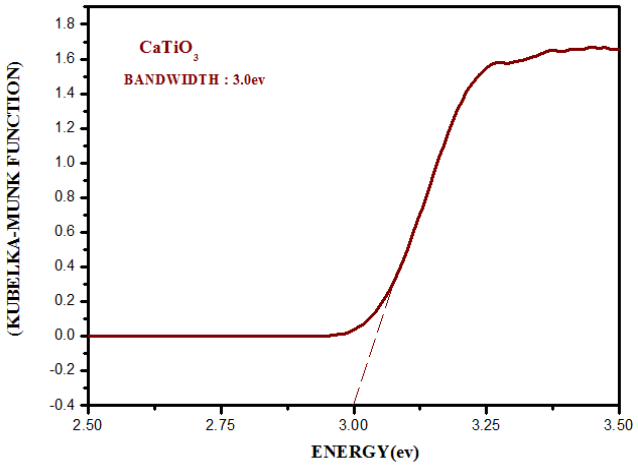

Fig .6. Optical band gap calculation of $CaTiO_3$ nanopowder prepared by sol-gel method

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3.6 High Resolution Transmission Electron Microsopy

The microstructure of $CaTiO_3$ nanopowder was examined by HRTEM. Fig 7a is the high –resolution image of $CaTiO_3$ nanopowder which exhibits the clear lattice fringes. The interlayer spacing 0.19nm is corresponds to (004) plane of $CaTiO_3$. Fig.7b shows the selected area electron diffraction (SAED) pattern of $CaTiO_3$ nanopowder calcined at 900^{o}C.

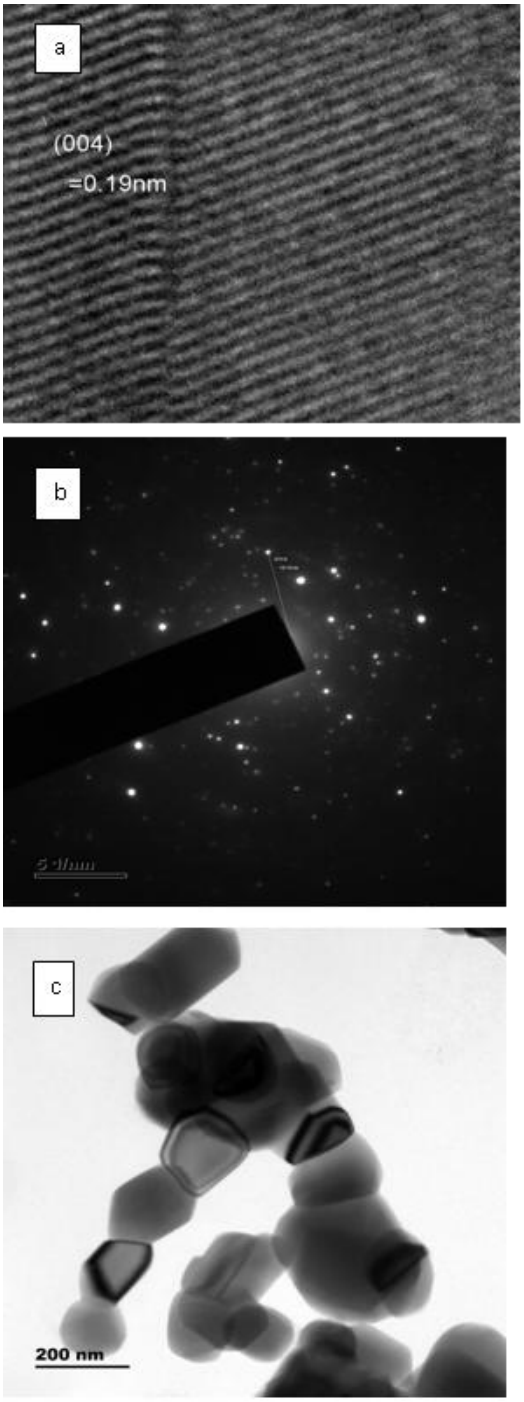

Fig . 7 a,b,c: HRTEM micrographs of $CaTiO_3$ nanopowder calcined at 900°C prepared by sol-gel method

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 $CaTiO_3$ nanopowder has not equal shape.

4. Conclusion

$CaTiO_3$ nanopowder prepared by using sol-gel method at low temperature calcinations . The sample was characterized by various advanced techniques. Particles were spherical in shape and the Particle size was varied from 26 - 31 nm, and the lattice parameters a, b. c are matched with JCPDS card no (88-0790).The functional group was analyzed by using FTIR analysis. The compositional analysis was analyzed by using EDAX analysis, it exhibits clear peaks of only Ca, Ti, and O elements. The band width is calculated from UV-VIS diffusion reflectance spectroscopy and it is 3.0ev. The interlayer spacing 0.19nm is corresponds to (004) plane of $CaTiO_3$.

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