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Synthesis of pristine $CrTiO_3$, Fe doped $CrTiO_3$ and Co doped $CrTiO_3$ with the structural and XRD studies

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Abstract: Numerous methods were reported in literature showing the possibilities of producing particle with size in the range of 2-100 nm. Among these methods some chemical techniques like the co-precipitation, the hydrothermal and the sol-gel methods which were reported to be fast and producing high quality nanoparticles. In this paper the preparation of chromium titanium oxide ,iron doped $CrTiO_3$ and cobalt doped $CrTiO_3$ by citric acid assisted sol-gel process.The X-ray diffraction characterization have been studied.The particle size were calculated using Williamson-Hall equation. From XRD some other structural parameters also determined.
Keywords: Chromium Titanium oxide, sol-gel method, particle size,X-Ray diffraction

Introduction

In the recent research the synthesis of nanoparticles and the study of it have much importance. Dimensionally, there are different types of nanomaterials such as zero-dimensional nanocrystals and nanoparticles, one-dimensional nano wires and nanotubes, and two-dimensional nanofilms and nanowalls[1]. The physical and chemical properties that are very much attracting the present science field when compared with the bulk material.The electronic and optical characteristic of metal nanoparticles are depending on size,shape etc. At small sizes, the properties vary irregularly and are specific to each size[2]. The control particle size,particle shape are important in nanoparticle preparation.One of the most important tool to study the nanoparticle is X-ray diffraction. In the present paper we discuss the simple and cheap preparation of chromium titanium oxide nanoparticle by co-precipitation method and XRD studies.

For the preparation of $CrTiO_3$ there are so many techniques[3] are available.Some of the major techniques are co-precipitation[4],hydrothermal[5]and sol-gel[6].Among these one of the suitable,simple and low cost method is sol-gel method and is mostly used in number of technologies [7,8]. In this paper we are investigating various parameters like particle size,peak indexing,d-spacing,full width at half maximum,volume and lattice strain from XRD data.

Experimental Details:

3.1 SAMPLE PREPARATION

Preparation of $CrTiO_3$

Nanoparticle sample of $CrTiO_3$ was prepared by sol-gel method. Stoichiometric amounts from pure raw materials of $CrNo_3$,$Ti(NO_3)_2$ and $C_6H_8O_7$ were used to prepare the required solution. The solutions of $CrNo_3$,6.27gm(50ml)and $Ti(No_3)_2$,(8.594gm in 50ml)were first mixed and stirring of 3000rpm for 30 minute. Add $C_6H_8O_7$ (5.764gm in 50ml)drop wise added to the solution and stirred again 15 minutes. Ammonia added drop by drop to obtain a mixture of PH 9 to 9.5.A specific amount of polyethylene glycol (10ml)used as surfactant was added to solution to get a gel form. Heat the colloidal solution at 80^0c for 30 minutes. After cooling 30 minutes the precipitate will get. The final product was washed with double distilled water several times and precipitation was achieved by addition of acetone to concentrated and removing the supernatant. Heat 150^0 in 30 minutes with hotplate and dried for 6 hours at muffle furnace.

Stoichiometric equation for the preparation for CrTiO3 is given below

$CrNo_3+Ti(No_3)_2+ C_6H_8O_7= CrTiO_3+4\ H_2O+6CO+1.5N_2+1.5O_2$

Preparation of $CrTi_{1-x}Fe_xO_3$ (x=0.5)

Nanoparticle sample of $CrTi_{0.5}Fe_{0.5}O_3$ was prepared by sol-gel method.Stoichiometric amounts from pure raw materials of $CrNo_3$,$Ti_{0.5}(NO_3)_2$,$Fe_{0.5}(NO_3)$and $C_6H_8O_7$ were used to prepare the required solution. The solutions of $CrNo_3$,6.27gm(50ml),$Ti(No_3)_2$ (7.39gm in 50ml)and $Fe(No_3)_2$ (4.45gm in 50ml)were first mixed and stirring of 3000rpm for 30 minute. Add $C_6H_8O_7$ (5.764gm in 50ml)drop wise added to the solution and stirred again 15 minutes. Ammonia added drop by drop to obtain a mixture of PH 9 to 9.5.A specific amount of polyethylene glycol (10ml)used as surfactant was added to solution to get a gel form. Heat the colloidal solution at 80^0c for 30 minutes. After cooling 30 minutes the precipitate will get. The final product was washed with

double distilled water several times and precipitation was achieved by addition of acetone to concentrated and removing the supernatant. Heat 150^0 in 30 minutes with hotplate and dried for 6 hours at muffle furnace.
Stoichiometric equation for the preparation for $CrTi_{1-x}Fe_xO3(x=0.5)$ is given below
$CrNo_3+Ti_{0.5}(No_3)_2+Fe_{0.5}(NO_3)+C_6H_8O_7= CrTi_{0.5}Fe_{0.5}O_3+4\ H_2O+6CO_2+2N_2$

Preparation of $CrTi_{1-x}Co_xO_3$ (x=0.5)

Nanoparticle sample of $CrTi_{0.5}Co_{0.5}O_3$ was prepared by sol-gel method.Stoichiometric amounts from pure raw materials of $CrNo_3$,$Ti_{0.5}(NO_3)_2$,$Co_{0.5}(NO_3)$and $C_6H_8O_7$ were used to prepare the required solution. The solutions of $CrNo_3$,6.27gm(50ml),$Ti(No_3)_2$ (7.39gm in 50ml)and $Co(No_3)$(4.57gm in 50ml)were first mixed and stirring of 3000rpm for 30 minute. Add $C_6H_8O_7$ (5.764gm in 50ml)drop wise added to the solution and stirred again 15 minutes. Ammonia added drop by drop to obtain a mixture of PH 9 to 9.5.A specific amount of polyethylene glycol (10ml)used as surfactant was added to solution to get a gel form. Heat the colloidal solution at 80^0c for 30 minutes. After cooling 30 minutes the precipitate will get. The final product was washed with double distilled water several times and precipitation was achieved by addition of acetone to concentrated and removing the supernatant. Heat 150^0 in 30 minutes with hotplate and dried for 6 hours at muffle furnace.
Stoichiometric equation for the preparation for $CrTi_{1-x}Co_xO3(x=0.5)$ is given below
$CrNo_3+Ti_{0.5}(No_3)_2+Co_{0.5}(NO_3)+C_6H_8O_7= CrTi_{0.5}Co_{0.5}O_3+4\ H_2O+6CO_2+2N_2$

Result and discussion

(1) peak indexing

From the peak positioning the unit cell dimensions are determined this process is called indexing which is the primary step in diffraction pattern analysis.Miller indices(hkl)
are necessary to be assigned for each peak to index.

Sample confirmation using JCPDS Data ($CrTiO_3$:33-0408)

Experimental Diffraction angle (2θ in degrees)	Standard diffraction angle(2θ) using JCPDS
41.41	41.025
54.505	54.628
62.947	62.782
84.32	84.188

From the above table it can be shown that the diffraction angle is exactly matches with the standard diffraction angle using JCPDS data.

(i) Powdered X-ray diffraction:

Structural identification was carried out by powder X-ray diffraction in a D8 advance bruker (germany) diffractometer using Cukα radiation and the diffraction angle were recorded in the 2θ ranged between 38˚- 80˚. The crystallite size and average particle size was calculated from the Debye Scherrer formula[9] using the peak broadening of XRD peaks. The method of analysis has been also reported in literature[10]. The surface morphology and shape of the existing nanoparticles were investigated using the scanning electron microscope which has done by FEI quanta 200F instrument and the elemental analysis and the chemical composition of the sample was identified by energy dispersive X-ray analysis done with a bruker spectrometer.

The powdered X-ray diffraction pattern of $CrTiO_3$,Fe doped $CrTiO_3$and Co doped $CrTiO_3$which are synthesised by sol-gel technique has been represented in the fig 1. These samples are sintered at 600˚C for 2 hours (4 to 5˚C/minutes) in air atmosphere. The obtained $CrTiO_3$,Fe doped $CrTiO_3$and Co doped $CrTiO_3$ samples could be indexed to rhombohedral structure.The sharp and intense peaks from the XRD patterns reveals the formation of fine crystalline phase that exist in the compounds. And it is matched with standard JCPDS data card no: 33-0408 for $CrTiO_3$. The distinctive diffraction peaks of of $CrTiO_3$,Fe doped $CrTiO_3$and Co doped CrTiO3 exhibits standard peak at 2θ values such as 28, 36, 41, 54, 70 are assigned to (110), (211), (210), (321), (432) planes respectively. From this XRD pattern it conforms that no extra peaks are identified which shows the formation of high purity nano crystalline compounds.

Fig .1. Powder XRD patterns of CrTiO3 ,$CrTi_{0.5}Fe_{0.5}O3$and $CrTi_{0.5}Co_{0.5}O_3$

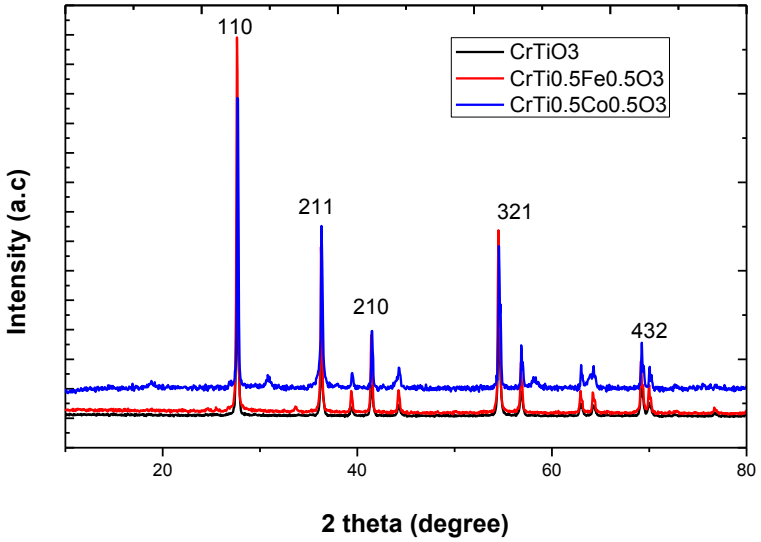


Table.1. Structural Parameters of $CrTiO_3$,$CrTi_{0.5}Fe_{0.5}O_3$and $CrTi_{0.5}Co_{0.5}O_3$

Compound name	2θ	Particle size D(nm)	Average particle size D(nm)	Particle size D(nm) W-H eqn	Volume (nm^3)	Lattice strain(ε) 10^{-4}	Interplanar spacing d(A^0)	hkl values	FWHM (rad)
$CrTiO_3$	41.41	9.251	10.17	10.5	0.0872	6.92	2.1318	210	$1.28x10^{-2}$
	54.505	9.734		11		5.46	1.6837	321	
	62.947	10.1		12.2		4.78	1.42727	310	
	84.32	11.6		13.2		2.799	1.14	432	
$CrTi_{1-x}Fe_xO_3$(x =0.5)	41.41	9.25	9.834	11.6		7.32	2.1318	210	$8.03x10^{-3}$
	54.50	9.734		11.4		4.4	1.684	321	
	62.94	10.146		12.11		4.25	1.427	310	
	84.62	10.207		14.3		3.92	1.076	432	
$CrTi_{1-x}Co_xO_3$(x =0.5)	41.518	9.255	9.710	11.5		11	2.17	210	$6.3x10^{-3}$
	54.55	9.736		12.1		8.5	1.68	321	
	62.99	10.14		12.5		6.46	1.42	310	

The average particle size (grain diameter)[11]were calculated from Debye-Scherrer formula,

$$D=0.9\lambda/\beta\cos\theta \quad (1)$$

where λ is the X-ray wavelength,β is the full width half maximum intensity value and θ is the bragg's angle. The average particle size were calculated as 10.17 nm for $CrTiO_3$, 9.83nm for $CrTi_{0.5}Fe_{0.5}O_3$ and 9.710nm for $CrTi_{0.5}Co_{0.5}O_3$.Particle size calculation by Debye-Scherrer formula is exactly matches with the particle size calculation by William –Hall equation[12].

Lattice strain(ε) calculated from Williamson-Hall equation given by

$$\beta\cos\theta=K\lambda/D+4\varepsilon\sin\theta \quad (2)$$

where λ is the X-ray wavelength, D is the particle size and θ is the bragg's diffraction angle.

The lattice parameters,unit cell volume were calculated using the following formula

$$\text{Volume } V=a^3\sqrt{(1-3\cos^2\alpha+2\cos^3\alpha)} \quad (3)$$

Using the XRD data the lattice parameter and various structural parameters such as crystallite size, volume, lattice strain, FWHM [13]also were calculated which are shown in table 1.

Particle size determination(D)

$CrTiO_3$

1)2Θ =41.41, θ =20.705
D=0.94x1.54x10^{-10}/(0.96xcos(20.705))
=9.251nm
2)2 Θ =54.505,θ =27.25
D=0.94x1.54x10^{-10}/(0.96xcos(20.705))
=9.251nm
3)2 Θ =62.947,θ =31.47
D=0.94x1.54x10^{-10}/(0.96xcos(31.47))
=10.1nm
4)2 Θ =84.32,θ =42.16
D=0.94x1.54x10^{-10}/(0.96xcos(42.16))
=11.6nm
Mean particle size(D)=10.171nm
Similarly we can find the particle size of other two samples.

Calculation of interplanar spacing(d)
nλ=2dsinθ (4)
where eqn (4) called Bragg's law.
$CrTiO_3$
1. d=nλ/2sin Θ
n=1,λ=1.54A^0 ,θ=20.705
=2.1318A^0
2. d=n/2sin Θ
n=1,λ=1.54 A^0,θ=27.2525
=1.6837A^0
3. d=nλ/2sin Θ
n=1, λ =1.54A^0 ,θ=31.47
=1.4272A^0
4. d=nλ/2sin Θ
n=1, λ =1.54A^0 ,θ=42.17
=1.1491A^0
Similarly we can calculate the interplanar spacing of the other two sample.

Fullwidth at half maximum(FWHM)
$\beta=(\theta_2-\theta_1)\pi/180$ radian (5)

$\underline{CrTiO_3}$
1)β=(41.860-41.108) π/180
=0.01318 radian

2) β =(55.061-54.149) π/180
=0.01590 radian

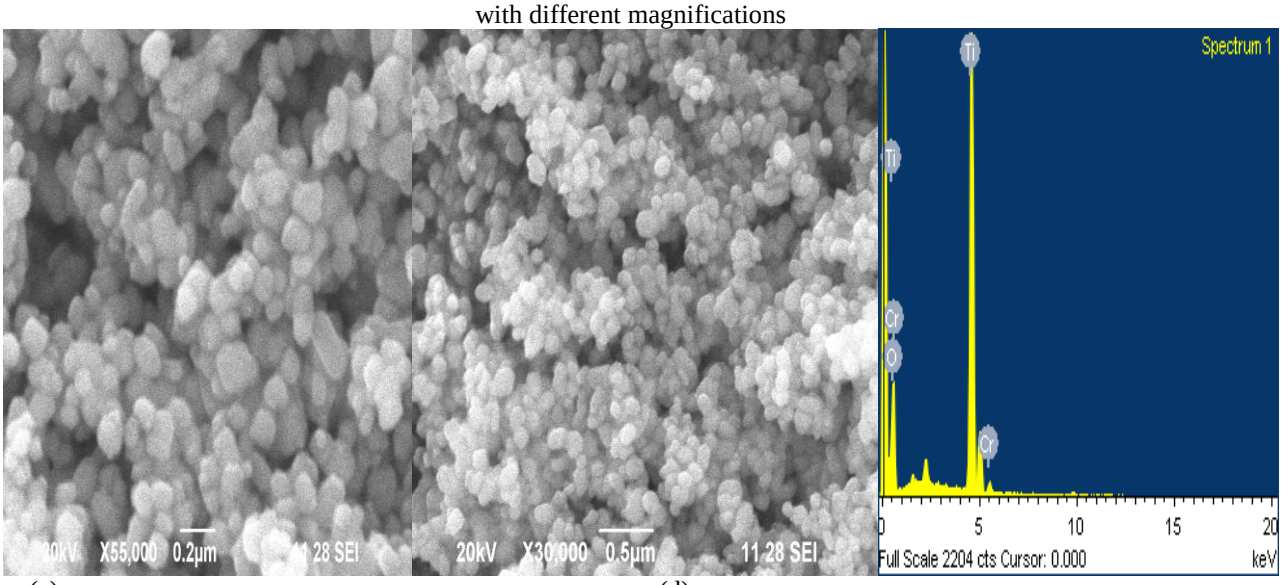
3) β= (63.42-62.699) π/180
=0.01257radian

4) β =(84.724-84.176) π/180
=0.00955 radian
Mean β=0.0128 radian
Similarly we can calculate the FWHM of the other two sample.

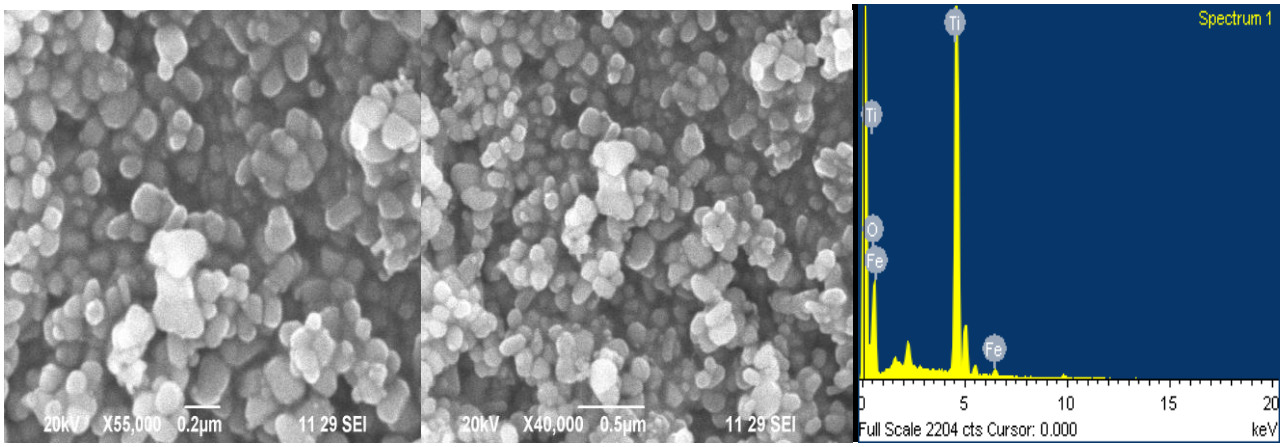
(ii) SEM and EDS analysis:

The surface morphology of the prepared samples are presented in fig(a) , (b),(c) also it shows the SEM images CrTiO3 ,$CrTi_{0.5}Fe_{0.5}O_3$and $CrTi_{0.5}Co_{0.5}O_3$ crystalline powders synthesised by co precipitation method[14] at different magnification from 0.2μm to 0.5μm respectively. This techniques is used to see the surface morphology and distribution of synthesised particle lying in micro to nano level.It clearly shows that an exact formation of ideal spherical $CrTiO_3$,Fe doped $CrTiO_3$and Co doped $CrTiO_3$ nanoparticles.

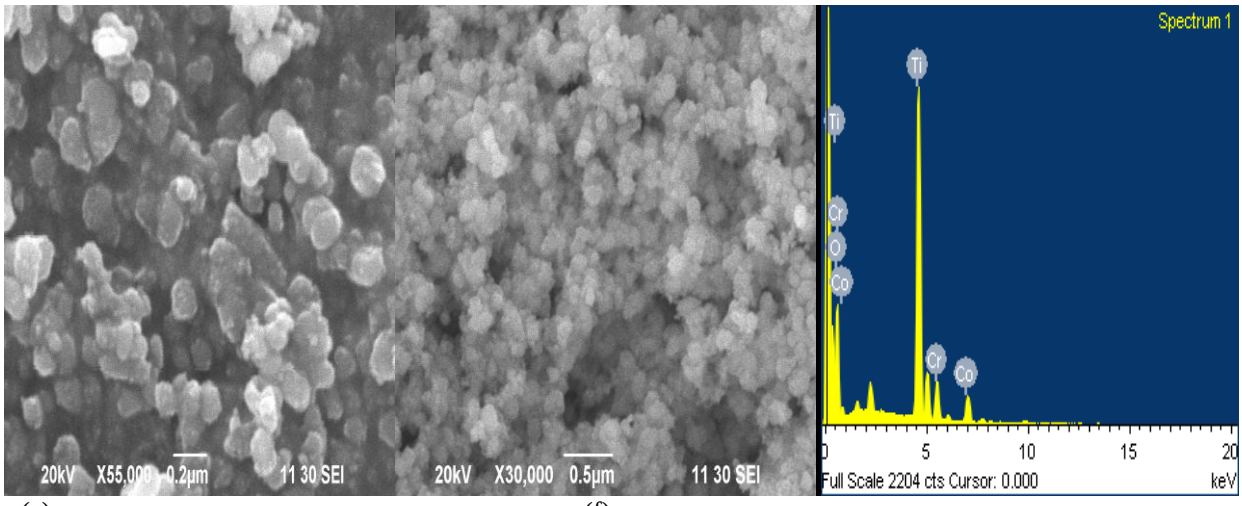
Figure 2 SEM images and EDX spectrum for (a) $CrTiO_3$, (b) $CrTi_{0.5}Fe_{0.5}O_3$ and (c) $CrTi_{0.5}Co_{0.5}O_3$ nanoparticles with different magnifications



(a) (d)



(b) (e)



(c) (f)

These analyses show that by using a moderate citric acid sol-gel technique [15]was highly suitable for the synthesis of ternary mixed metal oxide spherical nanoparticles. As compared with 0.2µm SEM images of

$CrTiO_3$, $CrTi_{0.5}Fe_{0.5}O_3$ and $CrTi_{0.5}Co_{0.5}O_3$ has very good structural confinement effect prepared by sol-gel technique. In order to show the elemental analysis and chemical composition of the prepared samples, the EDS spectra has also been included which are shown in fig 2 (d),(e) and (f). No unwanted peaks or impurity except as taken elements were observed in EDS spectra, which reveals the purity of $CrTiO_3$,Fe doped $CrTiO_3$and Co doped $CrTiO_3$ nanoparticles.

The atomic , weight % and intensity of the samples with corresponding stochiometry values of the existing Cr,Fe, Co and O elements.

Table2:sample with its constituting elements

Compound name	element	weight	Atomic percentage	Intensity
$CrTiO_3$	O(k)	54	77.9	0.3807
	Ti(k)	44	21.34	0.894
	Cr(k)	1.71	0.76	0.796
$CrTi_{1-x}Fe_xO_3(x=0.5)$	O(k)	52.8	77.0	0.366
	Ti(k)	46.0	22.42	0.834
	Fe(k)	1.19	0.52	0.825
$CrTi_{1-x}Co_xO_3(x=0.5)$	O(k)	2.09	75.51	0.451
	Ti(k)	1.58	18.83	0.910
	Cr(k)	0.42	3.08	0.823
	Co(k)	0.49	2.58	0.825

Conclusion

- CrTiO3,Fe doped and Co doped CrTiO3 nanoparticles were prepared using a citric acid assisted sol-gel technique.
- The synthesis process in this study are simple and easy to achieve the desized particle size distribution
- From the obtained XRD patterns, we have calculated structural parameters.
- XRD investigation showed that the synthesized compounds are in rhombohedral structure.
- Then, we identified no further elements are present in the EDS spectrum showed the formation of pure $CrTiO_3$,Fe doped and doped $CrTiO_3$ compounds.

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