

Original Research Article

Synthesis and structure-property relations in $\text{Ce}_{4-x}\text{Ca}_{1+x}\text{Fe}_{5-x}\text{Zn}_x\text{O}_{14+\delta}$ ($0 \leq x \leq 0.45$) (T1-T4: $x=0, 0.15, 0.30$, and 0.45) oxide systems.

Abstract

Synthesis of the composition $\text{Ce}_{4-x}\text{Ca}_{1+x}\text{Fe}_{5-x}\text{Zn}_x\text{O}_{14+\delta}$ ($0 \leq x \leq 0.45$) (T1-T4: $x=0, 0.15, 0.30$ and 0.45) were done via nitrate-citrate gel route. The wavelength of X-rays is on the atomic scale, so X-ray diffraction (XRD) is a primary tool for probing structure of nano-materials. Crystalline materials give rise to the most obvious applications, but there is also important information to be obtained from semicrystalline and even amorphous materials. XRD (X-ray diffraction) studies shows formation of single phase material. EDX analysis shows the decrease in density and decrease in unit cell volume for all the samples. EPR (Electron paramagnetic resonance) studies show two g-values. The lower value of $g \sim 1.99$ is attributed to the Fe^{3+} ion octahedral environment while the $g \sim 2.82$ is due to Ce^{3+} ions in the samples. The optical curves shows peak at ~ 583 nm due to simultaneous presence of both Fe^{3+} and Fe^{2+} inter-valence charge transfer electronic transition band. SEM shows the increasing porosity of samples from T1-T4.

Key words: nitrate-citrate gel, charge transfer

Introduction

Nanomaterials are being developed from almost every type of material-including polymers, metals, ceramics, composites, and biomaterials. In recent years there has been increasing emphasis on materials applicable to biomedical areas¹⁻³. Biomaterials are synthetic materials used to replace parts of a living system from a biological material, such as bone, that is produced by a biological system. Bioactive materials elicit specific biological responses at the interface of the material with the biological tissue which results in the formation of a bond between the living part and the material. Nanocomposite materials with nanoscale separation of phases improve the macroscopic properties of products. Magnetic multilayered materials are one of the most important aspects of nanocomposites as they have led to significant advances in storage media. They are either multilayer structures or inorganic/organic composites. Multilayer structures are typically formed by gas phase deposition or from the self-assembly of monolayers. Inorganic/organic composites are made by sol-gel techniques, bridging between clusters, or by coating nanoparticles. Rare earth elements and their compounds are useful for wide variety of applications⁴⁻⁷ in chemistry and materials science. The rare earth compound with the elements

32 exhibiting several oxidation states find uses as catalysts^{8,9} laser materials and other materials that
 33 make use of their magnetic properties¹⁰, considering the wide variety of applications and
 34 potentialities of the rare earth doped transition metals to understand their structure and physical
 35 properties. CeO based systems used to photo sensitive glass as a catalyst to polish glass and
 36 stone, Fe₂O₃ containing systems exhibit interesting electrical conductivity. In this paper, we
 37 report the structure-property relations in Ce_{4-x}Ca_{1+x}Fe_{5-x}Zn_x O_{14+δ} (0 ≤ x ≤ 0.45) oxide systems.
 38 Structural characterization of these samples was performed using Philips X-Ray diffractometer
 39 with Cu as the anode material. For the present study, XPERT-PRO diffractometer system with
 40 copper anode having Kα of 1.54060 Å was used the x-ray tube was operated at 25 mA/ 40 kV
 41 with 1000 watts x-ray power. The EPR experiments at room temperature and liquid nitrogen
 42 temperature were performed on an X-band JEOL-JES-TE 100 ESR spectrometer system with
 43 100 KHz field modulation and a phase sensitive detector to obtain first derivative signal. Quartz
 44 sample tubes were used for recording the EPR spectra. The g factor can be computed directly
 45 from the spectra using the recorded value of the frequency and the field position.

46 Experimental

47 Reagent grade chemicals are obtained from Qualigens fine chemicals and were used as such.
 48 Required amounts of calcium nitrate Ca(NO₃)₂, ferric nitrate Fe(NO₃)₃ and zinc nitrate were
 49 taken. Ammonium ceric sulphate (NH₄)₄Ce(SO₄)₄.2H₂O is converted into their nitrate by treating
 50 with calculated amount of Barium nitrate Ba(NO₃)₂ solution. All precursor solutions are then
 51 diluted to 0.1M solutions. The solution thus obtained was stirred for half an hour using magnetic
 52 stirrer, to get homogenous solution. 40 ml of 1M citric acid was then added as the complexating
 53 agent. The stirring was continued for two more hours. The PH of the solution was then adjusted
 54 to 1. The solution was then allowed to evaporate slowly with continuous stirring to form the gel.
 55 The gel was then decomposed to coarse powder by heating in an air oven kept at 120⁰ c for 2
 56 hours, and at 450⁰ c for 30 minutes in furnace. The black colour powder material thus obtained is
 57 sintered at 850⁰ for 6 hours and quenched in air. The powder XRD of the samples was recorded
 58 on a Rikagu Miniflex x-ray diffractometer using Cu k_α radiation in the range 5⁰ to 80⁰ in 2θ. The

EPR experiments at RT and LNT were performed on x-band JEOL-JES-TE100 ESR spectrometer system with 100KHZ field modulation. SEM provides topographical and elemental information at magnifications of 10x to 100,000x. Features seen in the SEM image then analyzed for elemental composition using EDX. Then energy dispersive x-rays (EDX) analysis was done with super Dryer –II model analyzer. The room temperature optical absorption spectra in the 200-800 nm region was measured by using a UV-visible spectrometer (variance model: 5000).

Results and Discussion

Fig1. Shows the XRD patterns of samples T1-T4. The powder XRD pattern of T1-T4 shows formation of single phase material. The XRD patterns for all the compositions are similar and the predominant peaks appear at similar and diffraction angle. This indicates that the lattice types of all the compositions are same. The XRD data were analyzed by using Treor 90 and the obtained unit cell parameters are given in Table1. Unit cell for all the samples T₁-T₄ were found to be monoclinic with lattice parameters a=9.6972, 10.1508, 6.7740, 8.1960Å⁰; b=6.2746, 3.9969, 5.3173, 4.0631Å⁰; c=5.2032, 4.6841, 5.9709, 5.7079Å⁰ and β =103.21, 98.02, 120.61 and 102.15 respectively. The volume of the unit cell is decreasing from 308.21Å³ for the composition T1(x=0) to 185 Å³ for the composition T3(x=0.430) and then increases for the composition T4(x=0.45). XRD peaks of all samples produce appreciable diffraction broadening and it is reasonably assumed that this arises from crystallite size. The crystallite size of the prepared compositions was calculated using Debye – scherrer formula¹¹. The particle size was found to be in the range 9.3289 nm-36.5131 nm.

Table .1. Unit cell parameters for the sample compositions of T1-T4 Ce_{4-x}Ca_{1+x}Fe_{5-x}

Zn _x O _{14+δ} (0≤x≤0.45)									
Sample No	Unit Cell	a	b	c	α	β	γ	Unit Cell Volume (Å ³)	
T1	Monoclinic	9.6972	6.2746	5.2032	90	103.21	90	308.21	
T2	Monoclinic	10.1508	3.9969	4.6841	90	98.02	90	188.18	
T3	Monoclinic	6.7740	5.3173	5.9709	90	120.61	90	185.09	
T4	Monoclinic	8.1960	4.0631	5.7079	90	102.15	90	185.82	

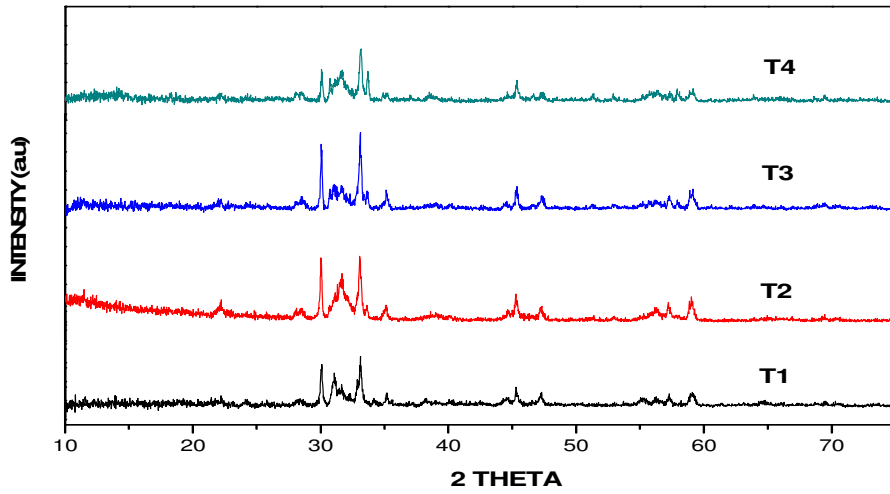


Fig.1. XRD Pattern for the sample compositions of T1-T4 $\text{Ce}_{4-x}\text{Ca}_{1+x}\text{Fe}_{5-x}\text{Zn}_x\text{O}_{14+\delta}$ ($0 \leq x \leq 0.45$)

Fig 2 and 3 shows the EPR line shapes measured at LNT (77K) and RT(300k) for the sample composition T1-T4 respectively. EPR studies carried out at RT reveals that there are two g-values, 1.981 ± 0.032 and 2.825 ± 0.041 , attributed to octahedral Fe^{3+} ion and Ce^{3+} respectively. The observed g-values in the range 1.980 ± 0.032 indicates the crystal-field effects on the 3d orbitals in the octahedral coordination^{12,13}. The observed g-values do not show any remarkable variation with x, this suggests that the symmetry around Fe^{3+} ion is same in all the samples. The observed g-value for cerium ion is in the range 2.825 ± 0.0414 . The high g-value-2.82 is attributed to spin orbit coupling. EPR measurements at 77k give g-value in the range 2.0517 ± 0.0102 . This g-value corresponds to octahedral $[\text{Fe}^{3+}\text{O}_6]^{-9}$ units in these samples. The observed g-value of 4.8990 and 4.9687 for the sample compositions T1 and T2 indicates the presence of tetrahedral $[\text{Fe}^{3+}\text{O}_4]$ units in these compositions. The sample compositions T3 and T4 shows smeared out line shapes. This indicates the formation of highly mobile electrons in the matrices. The values are given in table 2.

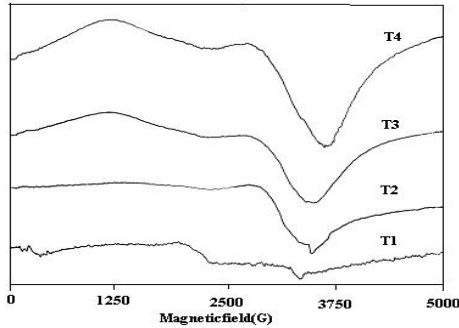


Fig.2 EPR lineshapes at 77 K of the samples T1-T4

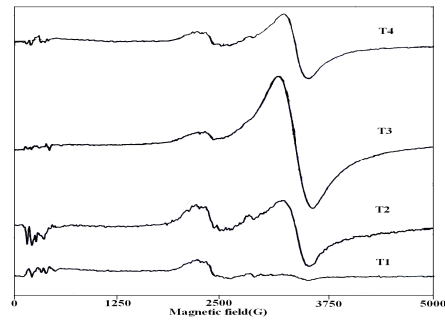
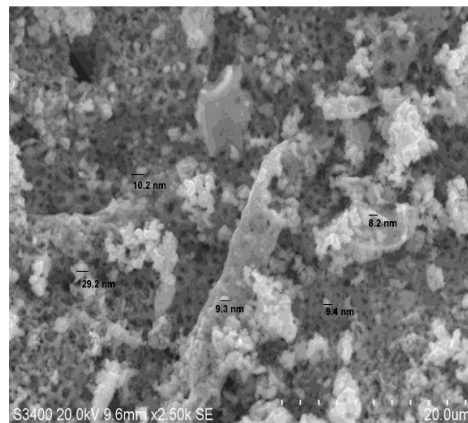
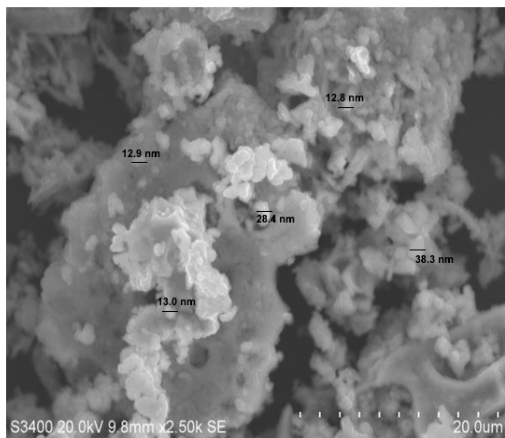


Fig.3 EPR lineshapes at 300 K of the samples T1-T4

Table 2. g-values of the sample compositions of T1-T4 $\text{Ce}_{4-x}\text{Ca}_{1+x}\text{Fe}_{5-x}\text{Zn}_x\text{O}_{14+\delta}$ ($0 \leq x \leq 0.45$) system

Sample No.	g-value at 298K		g-value at 77K	
	$g_{\parallel}$	$g_{\perp}$	$g_{\parallel}$	$g_{\perp}$
T1	2.8442	1.9567	4.8990	2.0943
T2	2.8605	1.9871	4.9687	2.0836
T3	2.8605	2.0179	5.4649	2.1501
T4	2.8300	2.0028	5.3003	2.0777

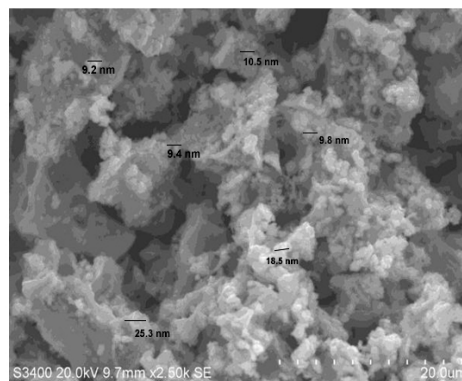
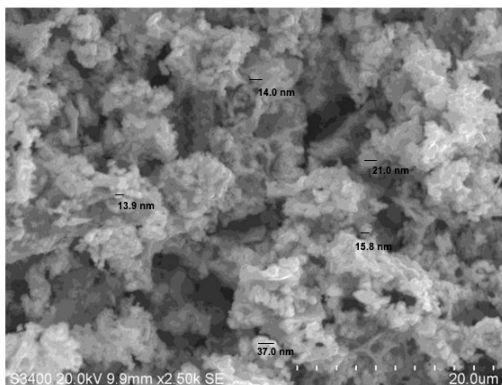
SEM images of the prepared samples at different magnifications are given in the Fig4 (a-d). The SEM images clearly show that the samples are becoming porous from T1-T4. Fig5 (a-d) shows the energy dispersive x-ray (EDX) profiles for the randomly selected particles of samples T1-T4. The EDX analysis results show the presence of elements in the sample in agreement with the starting materials. The EDX data are also in agreement with the expected stoichiometry. Fig 6(a-b) show the calculated and the experimental optical absorption spectra of samples T1-T4 respectively. On comparing figures we can see the perfect matching of theoretical prediction and experimental verification. Intense absorption around 230 nm in 6.a may be attributed to the charge transfer transitions. The peak at 583 nm may be due to simultaneous presence of both Fe^{3+} and Fe^{2+} intervalence charge transfer electronic transition band^{4,7}. The peak at 753 nm may be assigned due to transition of $6A1g(s) \rightarrow 4T1g(a)$ state of Fe^{3+} ion. The presence of peak at 230 nm confirms the octahedral symmetry around at Fe^{3+} ion. The observed bands (280, 300 and 352 nm) are assigned to be the transition $4f^1 2f_{5/2} - 5d^1(^2T2g)$ of Ce^{3+} .



(a)

(b)

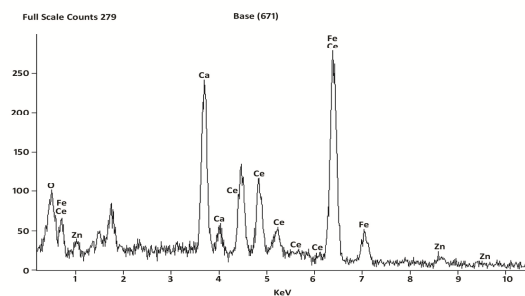
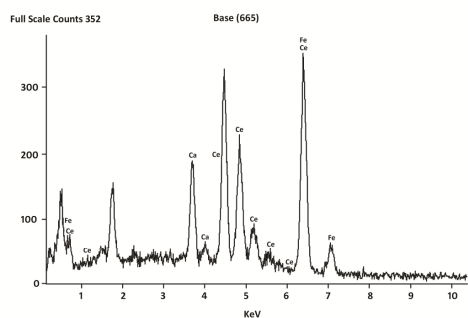
Fig 4. SEM Image of the sample composition a) $\text{Ce}_4\text{Ca}_1\text{Fe}_5\text{O}_{14+\delta}$ b) $\text{Ce}_{3.85}\text{Ca}_{1.15}\text{Fe}_{4.85}\text{Zn}_{0.15}\text{O}_{14+\delta}$



(c)

(d)

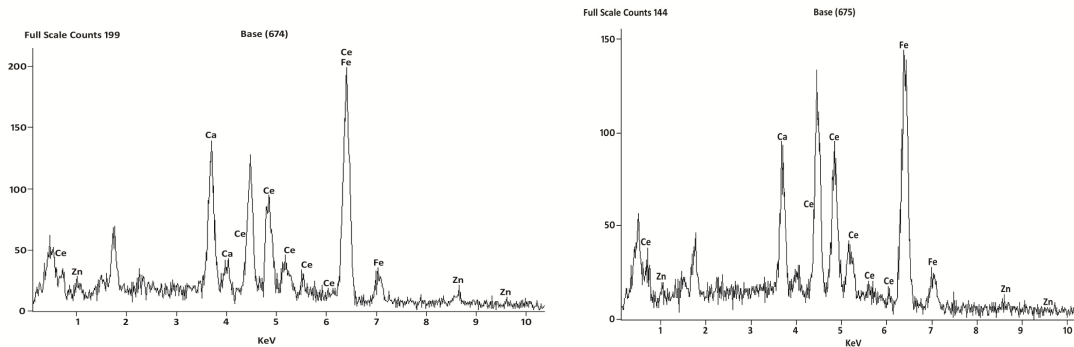
Fig 4. SEM Image of the sample composition c) $\text{Ce}_{3.70}\text{Ca}_{1.30}\text{Fe}_{4.70}\text{Zn}_{0.30}\text{O}_{14+\delta}$ d) $\text{Ce}_{3.55}\text{Ca}_{1.45}\text{Fe}_{4.55}\text{Zn}_{0.45}\text{O}_{14+\delta}$



(a)

(b)

Fig. 5. EDX Profile of the sample composition a) $\text{Ce}_4\text{Ca}_1\text{Fe}_5\text{O}_{14+\delta}$ b) $\text{Ce}_{3.85}\text{Ca}_{1.15}\text{Fe}_{4.85}\text{Zn}_{0.15}\text{O}_{14+\delta}$



(c)

(d)

Fig. 5. EDX Profile of the sample composition c) $\text{Ce}_{3.70}\text{Ca}_{1.30}\text{Fe}_{4.70}\text{Zn}_{0.30}\text{O}_{14+\delta}$ d) $\text{Ce}_{3.55}\text{Ca}_{1.45}\text{Fe}_{4.55}\text{Zn}_{0.45}\text{O}_{14+\delta}$

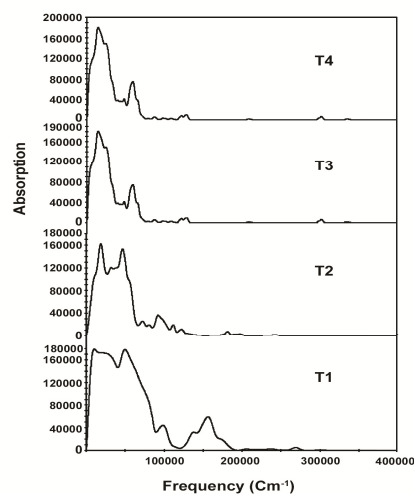
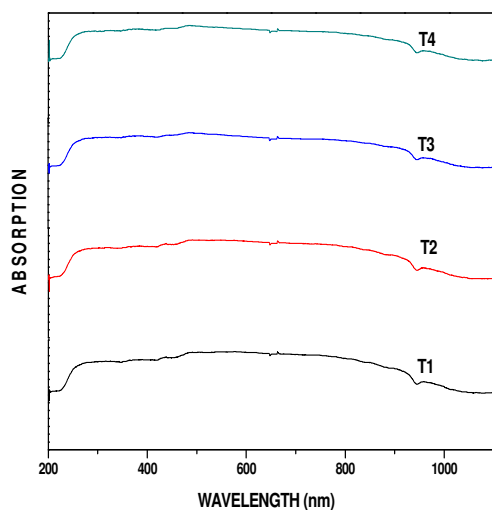


Fig. 6 a Experimental optical absorption plots of T1-T4

Fig. 6 b CASTEP calculated absorption plots of samples T1-T4

Conclusion

Powder XRD data for the samples shows formation of single phase material. EPR studies carried out at RT shows two g-values. The lower g-value 1.99 is attributed to the Fe^{3+} ion octahedral environment and g 2.82 is attributed to Ce^{3+} ions in the samples. EPR measurements at 77k shows smeared out line shapes which indicate the formation of mobile electrons in the matrices. The peak with g 2.08 is retained with an additional peak around g 4.98 in T1 and T2. The g-value around 4.98 in T1 and T2 is due to the presence of $[\text{Fe O}_4]^{5-}$ tetrahedra in these samples. The absence of hyperfine features in the line shapes at 77 and 300 k of samples T1 and T2 is due to very rapid spin-lattice relaxation of Ce^{3+} ions in the lattice. EDX analysis results showed that the

presence of elements in the samples is in agreement with the starting materials. The optical curves shows peak at 583 nm may be due to simultaneous presence of both Fe^{3+} and Fe^{2+} intervalence charge transfer electronic transition band. The peak at 753 nm may be assigned due to transition of $6A_{1g}(s) \rightarrow 4T_{1g}(a)$ state of Fe^{3+} ion. The presence of peak at 230 nm confirms the octahedral symmetry around at Fe^{3+} ion. The observed bands (280, 300 and 352 nm) are assigned to be the transition $4f^1 2f_{5/2} - 5d^1(^2T_{2g})$ of Ce^{3+} .

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181

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