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Role of Fe doping on surface morphology, electronic structure and magnetic properties of Fe doped CeO_2 thin film

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ABSTRACT

The electronic structure and magnetic properties of $Ce_{0.95}Fe_{0.05}O_2$ thin film (Fe-CeO₂ TF) were studied in the present work. The fabrication of 5% Fe-CeO₂ TF on the LaAlO₃ (LAO) (h00) substrate was performed using pulsed laser deposition (PLD) technique at 200mTorr oxygen partial pressure. Carefully deposited films were characterized through x-ray diffraction (XRD), atomic force microscopy (AFM), near edge x-ray absorption fine structure (NEXAFS) spectroscopy, and dc-magnetization measurements. XRD results indicated the polycrystalline nature of the film and showed that the film was grown along (220) preferred orientation. The AFM analysis revealed that the average surface roughness was found to increase for Fe-CeO₂ TF as compared with undoped CeO₂TF. The NEXAFS spectral analysis revealed the formation of oxygen vacancies because the reduction of valence state of Ce is known to be accompanied with generation of oxygen vacancies. The dc-magnetization measurements showed room-temperature ferromagnetism in the doped films with Tc = ~ 300 K.

1. Introduction

The emerging spintronic-based technology like non-volatile memory, nano-electronics etc has opened doors for researchers to exploit the magnetic traits of the dilute magnetic semiconductors (DMS) and other systems like (Ga, N) Mn, NiF, Mn₂Sn, Ni₂MnGa etc [1–13]. Highly dense thin films of such materials have also gained attention due to their potential applications in magneto-optical devices. These prospects have motivated the researchers to search new materials which can be utilized to manufacture modern-day spintronic devises. Lately, the interest has been developed in the investigation of CeO₂ TFs, because reduced CeO₂ surface acquires plenty of mixed Ce states (Ce³⁺/Ce⁴⁺), enough to make a material ferromagnetic [14]. A number of previous findings have associated the reduction of valence state of Ce with the creation of oxygen vacancies which participate in the spin localization, and upsurge the density of states at fermi level. This acquaints the CeO₂ with significant magnetic moment which may enable it to become a functional material for spintronic applications such as data storage, spin valves, sensors, non-volatile magnetic memory etc. [15]. Alongside, CeO₂ has widely been considered as a potential candidate for the constructive improvement in the surface properties due to their easy reducibility. As a matter of fact, ceria is a very interesting material in terms of their properties like oxygen storage capacity, high dielectric constant ($\epsilon = 26$) etc. It exhibits quickly interchangeable dual valence states by undergoing oxidation and reduction processes that can be utilized expediently to manipulate the properties like structural, optical, magnetic and many other [16]. In the pure form, CeO₂ possesses cubic fluorite structure that upholds the stoichiometric deviations. This proves to be advantageous when CeO₂ is doped with small fraction of transition metal ions, they are anticipated to enhance their properties without distorting the original structure. Hence, transition metal doped CeO₂ constitute a prospective dilute magnetic semiconductor (DMS) oxide that might be utilized in various above-mentioned applications. There are numerous speculations behind the actual cause of augmentation of properties of transition

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metal doped CeO₂. Several groups of researchers have synthesized different structures of pure and transition metal doped CeO₂ and investigated their properties for significant modifications [17]. Chuanhui Xia et al. have synthesized and analysed Mn doped CeO₂ nanorods and determined enhanced magnetization and photo absorption [18]. Likewise, oxygen storage capacity has been found to be enhanced in ultrathin films of CeO₂ as reported by Gopal Balaji et al. [19]. Similarly, doping of transition metal ions into CeO₂ matrix have been found to optimize the various properties of CeO₂ [20–22]. Hence, these reported works ascertain that the doping of transition metals in CeO₂ nanostructures enhance their properties.

Moreover, out of the various structures, thin films have been considered of great significance due to their high surface to volume ratio, densification, and formation of ideal grain boundaries. The welldefined grain boundaries develop a good interface microstructure for the domain formation which determines the ferromagnetic characteristics of the material. Whereas, high surface to volume ratio allows the accumulation of the heavier ions on the surface disposing it for reactions. Besides, these investigations have also found the traces of oxvgen vacancies in the samples and thereby approving them as the foremost cause of the enhancing properties of the material. In CeO₂, the formation of oxygen vacancies leads to the reduction of cerium from +4(CeO₂) state to +3 (Ce₂O₃) state, where Ce³⁺, being bigger ions, floats onto the surface as a common behaviour. Therefore, the creation of oxygen vacancies not only enhances the oxygen storage capacity of the material but also enhances the efficiency of the surface to react with the surrounding environment. In addition, the easy exchange of oxidation states from +4 to +3 in CeO₂ due to unoccupied 4f states, makes this compound more susceptible to the oxygen vacancy formation. Furthermore, when a transition metal ion such as Fe^{2+} or Fe^{3+} is doped into CeO₂, it substitutes Ce⁴⁺ and liberates oxygen which may take the position in interstitial lattice sites probably because of smaller ionic state as well as the ionic size of Fe^{2+} (0.74 Å) as compared to that of Ce^{4+} (0.97 Å) [15,23–27].

Therefore, in order to understand the role of oxygen vacancies and transition metal ions on the materials properties, in this work, we have fabricated Fe doped CeO_2 thin films, with 5% concentration of Fe ions, on LAO [h00] substrate by PLD technique at 200mTorr oxygen partial pressure and employed with multiple characterization techniques for analyses. The growth of the thin films along a particular orientation have been studied using XRD. The surface morphology was studied through AFM. The NEXAFS spectroscopy study was done to investigate the change in the oxidation state of the Ce ions and the valence state of doped iron and the ferromagnetic response was measured using dc magnetization.

2. Materials and methods

The Fe-CeO₂ TF was grown on LAO (h00) substrate by using PLD technique. The bulk targets of circular shape with 2.5 cm in diameter were prepared by solid state reaction technique by applying a pressure of 5 tons. Thus, prepared pallets were sintered for 12 h at 1200 °C. After sintering, the pallets were used as the targets while growing the film inside the PLD deposition chamber. The high-density bulk targets were studied through XRD to determine the single-phase nature. The LAO substrates were sterilized using acetone and distilled water several times before the film deposition followed by heating for 1 h. The cleaned substrates were placed inside the vacuum chamber. The film target was fixed on a rotating holder at a distance of 5 cm from the substrate. The process took place at 200mTorr oxygen partial pressure. The target was kept rotating during the process in order to obtain uniform deposition. A pulsed excimer laser (KrF: $\lambda = 248$ nm) with a pulse duration of 20 ns and pulse repetition rate of 10 Hz was used to ablate the target. The temperature of the substrate was kept at 650 °C during deposition. After 30 min, when the film was deposited, the chamber was cooled down to room temperature at the rate of 5 °C/min.

After the successful growth, the films were studied through various characterization techniques. The single-phase polycrystalline nature was analysed through XRD with Cu-K α radiation ($\lambda = 1.5406$ Å) in θ -2 θ mode. Bruker Multimode 8 atomic force microscope was used to analyse the surface morphology. The AFM micrographs were analysed using Nanoscope 1.5. The magnetic response of the films was studied by commercial quantum design physical property measurement system (PPMS- 6000). The NEXAFS spectra were obtained at 10D XAS KIST (Korea institute of Science and Technology) beamline situated in Pohang Accelerator Laboratory (PAL) [28,29].

3. Results and discussion

3.1. XRD analysis

Fig. 1 displays the XRD patterns of 5% Fe-CeO₂ TF along with the patterns of LAO substrate. The XRD patterns show that Fe doped CeO₂ has grown on the LAO substrate with preferred orientations. The LAO patterns show two peaks designated by LAO (200) and LAO (300) belonging to the (h00) family of planes of LAO [30].

The peak positions, designated by F (111), F (200), F (220) and F (331), are in accordance with the pure CeO₂ which rules out the formation of any secondary phases [21]. This signifies that Fe^{2+} ions have well substituted the Ce⁴⁺ ions in the host lattice. The patterns of the film, further, show two peaks with significant intensity indicating polycrystalline nature of the film. These fine peaks indicate the good texturing of the film with a small value of FWHM (0.0486°) pointing towards utterly grown crystallites. The planer orientations of the film have been designated by F (hkl) which is consistent with cubic fluorite structure (Space group: Fm3m) of pure CeO₂ [31]. The peak F (220) exhibits maximum intensity, suggesting the preferred planer orientation of the deposited film along LAO (200) at a 2 θ value of 48°. The secondary peaks due to metallic iron, iron cluster or any other crystalline impurity have not been identified indicating single phase nature of the film. These outcomes suggest that the Fe ions have been completely diluted in the CeO₂ lattice with Fe²⁺ ions successfully substituted Ce⁴⁺ ions in the host lattice.

3.2. AFM analysis

Atomic force microscopy (AFM) is an excellent high-resolution surface imaging technique routinely used for topographic analysis of the



Fig. 1. XRD spectra of 5% Fe-CeO₂ TF and LaAlO₃ (LAO) substrate.

thin films. Here, we have used AFM imaging technique for studying the roughness of film due to its high resolution in nano-meter to the angstrom range. Before scanning the 1 μ m \times 1 μ m area, we have first scanned 10 $\mu m \times$ 10 μm area to confirm even surface coverage and to elude the contaminated area. Fig. 2(a-d) highlights the 2D and 3D micrographs obtained using AFM for undoped CeO₂ and Fe-CeO₂ TFs. The inset in Fig. 2(a-b) shows the AFM image obtained by scanning area of 1 μm imes 1 μm for undoped and Fe doped CeO₂ films. The surface morphology of films was recorded in tapping mode using commercial silicon cantilevers and all these micrographs were recorded in air. The AFM images show the dense, and uniform grain distribution. It can be seen from the AFM image that surface of undoped film is flat with nearly isotropic nano-sized islands. However, it is observed that the surface morphology of Fe doped CeO₂ films changed drastically. The AFM image of Fe doped CeO₂ film inferring a spindle like structure on the film surface, which might be formed due to the elongation of surface islands. Moreover, these spindle like structure on the film surface are not dispersed separately, but are connected and overlapped with each other, constructing a surface structure similar to interwoven twill [32]. The similar interwoven structures have been reported on the surface of CeO₂ films deposited on single crystal YZS (001) substrate using magnetron sputtering. Trtik et al. also observed similar interwoven structures morphology of CeO₂ thin film epitaxial grown on yttria-stabilized zirconia/Si(0 0 1) substrate [33].

Surface structure plays a very important role in defining the interactions of a material with its external environment, therefore, in order to compare the nanostructures on the surface, there is requirement of quantifiable, descriptive parameters. There are various parameters existing in the literature used for describing the roughness. However, it is found that mostly two of these parameters such as average surface roughness (R_a) and root mean square roughness (R_d) have been used to explain the roughness of the films. Here, in order to quantitatively evaluate roughness, we have used seven statistical parameters such as average surface roughness (R_a), root mean squared surface roughness (R_q), maximum surface roughness (R_{max}), surface area increase (R_{sa}), and peak counts (R_{pc}), for the topographic analysis of the undoped and Fe doped CeO₂ films. The remaining two parameters are R_{skw} and R_{kur} , which give the measure of skewness and kurtosis of the height distribution histogram. The higher values of R_{skw} and R_{kur} tell about the smoothening of the surface.

Among these parameters, the vertical dimensions of the surface have been defined using the roughness parameters R_a , R_q , and R_{max} , while the others (R_{sa} and R_{pc}) describe its horizontal dimensions which give information about the density of distribution of peaks.

The average value of the surface height variables $z(x_i, y_j)$ of grains with relative to the center plane is explained using roughness average (R_a). The roughness average at a particular point, the height $z(x_i, y_j)$ in an area contain $n \times n$ points, is defined as [28,34]:

$$R_a = \sum_{i,j=1}^{n} \left| \frac{z(x_i, y_j) - \langle h(x_i, y_j) \rangle}{n} \right|$$
(1)

where $z(x_i, y_j)$ represents the average of heights values and can be calculated as

$$\langle z(x_i, y_j) \rangle = \frac{1}{n} \sum_{i, j=1}^n z(x_i, y_j)$$
⁽²⁾

The standard deviation of the surface height within the given area and at a height z (x_i, y_j) of grains is represented by root mean square roughness (R_q). The RMS is defined as:



Fig. 2. Atomic force microscopy micrographs (a) 2D micrograph of undoped CeO₂ TF. Inset in Fig. 2(a) shows the high resolution micrograph of undoped CeO₂ TF. (b) 2D micrograph of Fe-CeO₂ TF. Inset in Fig. 2(b) shows the high resolution micrograph of Fe-CeO₂ TF. (C) 3D micrograph of undoped CeO₂ TF. (b) 3D micrograph of 5% Fe-CeO₂ TF.

$$R_{q} = \sqrt{\sum_{i, j=1}^{n} \frac{\left[h(x_{i}, y_{j}) - \langle h(x_{i}, y_{j})\rangle\right]^{2}}{n}}$$
(3)

The R_{max} is defined as the difference between the highest and lowest points on a surface and can be significantly affected by the surface damage or contamination. Various parameters calculated using the AFM analysis are shown in Table 1. It is observed that the Fe doped CeO₂ film shows the highest average R_a compare to the undoped film. Moreover, the R_a and R_{max} also followed the similar trend. Surface area difference (Rsa) was also determined to study the effect of Fe doping on the increase in the surface between the actual surface area and the projected area. It is observed that Fe doped CeO₂ film shows the largest increase in the surface area which is in analogues to the roughness parameters. The peak counts (Rpc) were also found to increase for Fe doped thin films, which indicates that the size of the peaks decreases with doping. Various parameters used to study the topography infer that the roughness increase with Fe doping in CeO_2 films. In addition, the values of R_{skw} and $R_{\rm kur}$ have been found to be reduced when CeO₂ matrix is doped with Fe ions. However, these values show an increase when area of observance is increased from 1 μ m imes 1 μ m–5 μ m imes 5 μ m. This shows that the skewness and kurtosis of the height distribution histograms depends strongly on the area of observance.

Furthermore, the particle density (not shown here) and roughness of the films have also been measured for an area of $1 \ \mu m \times 1 \ \mu m$ and $5 \ \mu m \times 5 \ \mu m$. Thus, the required parameters as proposed by Webb et al. [35] have been displayed in Table 1 which completely describes the surface properties of the deposited thin films. The parameters indicate that particle density has been found to increases with doping, whereas, it decreases as the area of observance increase. However, the area under consideration does not affect the roughness, but it has been found to enhance as a consequence of doping process. However, aside from the doping accomplishments, the experimental conditions during film deposition cannot be ignored which affect the surface roughness [35]. Nonetheless, for the similar deposition conditions, the dopant concentration has been found to not only affect the structural parameters but also the nature of the film surface.

3.3. NEXAFS analysis

In order to overcome the limitations of XRD analysis which is confined to the determination of purity and crystallinity of the material, NEXAFS spectroscopy analysis has been carried to extract comprehensive information about the absorbing ion as well as the slightest deviation in the electronic structure of the doped film. The NEXAFS spectroscopic technique is an effective method for the determination of the oxidation state, the local atomic structure and ligand environment around the probed ions in the DMS oxide systems. The edge energies of the NEXAFS spectra give information about the oxidation state of the absorbing ion. Hence, the changing edge energies reveal the changing oxidation state of the probed ion. The position and intensity of the spectral features provide acquaintance of the coordination number and

Table 1

Various atomic force microscopy roughness parameters such as: average surface roughness (R_a), root mean squared surface roughness (R_q), maximum surface roughness (R_{max}), skewness (R_{skw}), kurtosis (R_{kur}), surface area increase (R_{sa}), and peak counts (R_{pc}).

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	Scan area	R _a (nm)	R _q (nm)	R _{max} (nm)	R _{skw}	R _{kur}	R _{sa} (%)	R _{pc}
CeO ₂	1 μm ² 25 μm ²	1.21 5.32	1.71 8.16	23.5 59.8	2.72 2.45	3.83 9.26	0.63 2.26	134 549
Fe-	$1 \ \mu m^2$	1.38	1.74	8.6	0.24	4.03	5.29	1026
CeO ₂ TF	25 μm ²	6.60	9.42	62.0	2.11	7.23	2.60	1464

geometry of the compound [36–38].

Fe L_{3.2} edge: Fig. 3 shows the Fe L_{3.2} edge features of Fe-CeO₂ TF accompanied by the reference spectra of Fe₂O₃ and Fe₃O₄. The reference spectra of FeO has been shown in the inset of Fig. 3. The Fe $L_{3,2}$ edge spectra have been obtained as a result of the transitions from Fe $2p_{3/2}$ and Fe $2p_{1/2}$ orbitals respectively to Fe 3d orbitals in the range of 700 eV-750 eV which lies in between that of K and M edge transitions [39]. Further, the 2p core hole potentials with a short core-hole lifetime originate the splitting of L_3 and L_2 individual peaks into well-defined doublets t_{2g} and e_g labelled as a (708.4 eV), b (710 eV) and c (722 eV), d (723.4 eV), respectively. The short core-hole lifetime influences the broadening giving rise to sharp edges of the spectra. To find the oxidation state of Fe in the Fe -CeO2 TF, their spectra has been compared with those of reference spectra. It is be observed that the doublets of L_3 (a, b) and L_2 (c, d) are well separated in the spectra of Fe₂O₃ (Fe⁺³), whereas, in the spectra of FeO (Fe⁺²), the shoulder peak-a almost disappears. On the other hand, the spectra of Fe₃O₄ (Fe⁺²/Fe⁺³) resembles perfectly to that of the Fe-CeO₂ TF having same edge energies which indicates that Fe has been dissolved into mixed valence state into CeO₂ lattice. These outcomes further rule out the formation of any other phases of Fe or Fe clusters into Fe doped CeO₂ thin film.

Ce M_{5.4} edge: The Ce M_{5.4} edge spectra have been demonstrated in Fig. 4(a) in the energy range 870-910 eV along with that of undoped CeO₂. As we have investigated from Fe $L_{3,2}$ edge analysis that Fe has been dissolved into CeO_2 in mixed valence state which means that $Fe^{2+}/$ Fe³⁺ ions replace Ce⁴⁺ ions in the host lattice. Therefore, in Fe doped CeO₂, charge compensation must be provided necessarily. Besides it has been reported by various group of researchers that the substitution of a transition metal cation in place of a host cation causes the generation of oxygen vacancies [40]. These oxygen vacancies trap electrons and interact locally with Fe^{2+}/Fe^{3+} and Ce^{3+} in order to preserve the oxidation state of Ce to +4 in the lattice. The Ce $M_{5.4}$ - edge spectral features originate due to the transitions from Ce 3d core states to higher unoccupied Ce 4f states. The splitting of spectra into M_5 and M_4 edges has been caused by the crystal field splitting of Ce 3d into Ce $3d_{5/2}$ and $3d_{3/2}$. The M_5 and M_4 spectra peaks have been obtained at 880 eV and 898 eV with a splitting of 18 eV. The sharp edges can be easily viewed from the first derivative plot exhibited in the upper stack of Fig. 4(a). The first derivative provides the qualitative evaluation of the peak. Both



Fig. 3. Fe $L_{3,2}$ edge spectra of 5% Fe-CeO₂ TF along with reference spectra of Fe₂O₃ and Fe₃O₄; (inset: reference spectra of FeO).



Fig. 4. (a) Ce $M_{5,4}$ edge spectra of 5% Fe-CeO₂ TF along with reference spectra of undoped CeO₂; (b) O K edge spectra of 5% Fe-CeO₂ TF along with reference spectra of undoped CeO₂ (top stack: first derivative of the respective spectra); (c) Gaussian fit of Ce 4f states; (d) O K edge spectra of undoped CeO₂ and 5% Fe-CeO₂ TF along with reference spectra of FeO, Fe₂O₃ and Fe₃O₄.

the edges possess satellite structures of small intensity on the right side of the main peak with a difference of nearly 5 eV which may be evolved due to the weak transitions to Ce 4f antibonding states [29]. By comparing the spectra of Fe-CeO₂ TF with that of undoped CeO₂, it has been observed that spectral positions and the configurations of the two spectra resembles perfectly suggesting that the oxidation state of Ce remains +4 in the doped thin film. Therefore, it could be expected that the tetrahedral configuration of Ce in undoped CeO₂ has been preserved in Fe-CeO₂ TF.

O *K* edge: The O *K* edge spectra of Fe-CeO₂ TF has been displayed in Fig. 4(b) along with that of reference spectra of undoped CeO₂ in the energy range 520–550 eV. The graph is constituted of three stackslower, middle and upper. The well separated spectra of undoped and doped CeO₂ has been shown in lower stack. The middle stack shows the normalized spectra, while the upper stack shows the first derivative of both the samples. The spectral features arise due to the transitions from O *1s* core states to unoccupied Ce *4f*, *5d* states through hybridization with O *2p* states. The unoccupied Ce *4f* states constitute the bottom of the conduction band, while Ce *5d* states constitute the higher

unoccupied states of the valence band. The first peak labelled as a (526 eV) has been assigned to the transitions to Ce $4f^0$ states, while the next two peaks labelled as **b**₁ (529 eV) and **b**₂ (534 eV) have been assigned to the transitions to Ce 5d states which split into two peaks i.e. $5d-t_{2g}$ and $5d-e_{\alpha}$ states owing to crystal field splitting effects. These two distinct peaks $\mathbf{b_1}$ and $\mathbf{b_2}$ correspond to the transitions to $5d_{5/2}$ and $5d_{3/2}$ orbitals respectively [41]. It is realized here that the splitting in the spectra of undoped and Fe doped CeO2 is nearly same, therefore, crystal field effects are not likely to be dominated by the Fe doping. A small feature appears near 540 eV, is marked as c. Furthermore, the spectral configuration of O K edge spectra of Fe-CeO2 TF appears to be similar to that of undoped CeO₂ with a slight shift of 0.18eV. The complete resemblance of the spectra of Fe-CeO₂ TF to that of undoped CeO₂ indicates to the fact that majority of Ce ions are in +4 oxidation state in doped thin film. However, the slight increase in edge energy points towards the reduction in the oxidation state of a small concentration of Ce ions. This happens because when Fe^{2+}/Fe^{3+} ions of smaller ionic size and lesser oxidation state substitutes the Ce⁴⁺ ions in fluorite lattice, then the oxygen vacancies are created and the bound electrons get delocalized.

These delocalized electrons, further, either may get trapped into vacancies or may contribute to the conduction current. Thus, formation of oxygen vacancies leads to the reduction in valence state of small amount of the Ce ions in the host lattice.

Further, the first derivatives of the O *K*-edge spectrum of Fe-CeO₂ TF have been compared with that of the undoped CeO₂. The slightly reallocated absorption edges can be clearly seen indicating small reduction in the valence state of Ce. In addition, the intensity and peak width of the spectra of thin film has also been reduced with Fe doping which is clearly visible in the normalized spectra. Since the intensity of a NEXAFS spectra is a direct measure of the unoccupied states, the reduced intensity indicates towards the filling of unoccupied states in the conduction band, thereby revealing the reduction in the valence state of Ce and formation of oxygen vacancies in the host lattice.

The concentration of unoccupied Ce 4f states in conduction band can be determined by calculating the area under the curve of peak-**a** as shown in Fig. 4(c). In addition, a broad continuum spectral feature with negligible intensity have also been identified denoted by peak **c** (539 eV) which have been assigned to the transitions to extended unoccupied fstates in the top of the conduction band. Furthermore, we have also compared the spectra of Fe-CeO₂ TF with those of reference spectra of FeO, Fe₂O₃ and Fe₃O₄ as demonstrated in Fig. 4(d). No similarity in the peak positions or features was observed between the spectra of thin film and the reference compounds which lead to the rejection of the formation of Fe clusters or iron oxides in the film. These results are quite similar to some earlier reported results in which the NEXAFS analysis of O *K* edge have shown a little or no variation in the ligand structure of the host cation on doping with different elements [29,38].

3.4. dc - magnetization

The magnetic hysteresis loop of Fe-CeO₂ TF has been displayed in Fig. 5 which was recorded in the applied field range ±4000 Oe at 300 K. The saturation has been attained by the curve above 4000 Oe. The low field M-H loop is shown as inset in Fig. 5. The diamagnetic response of the substrate holder has been subtracted. The hysteresis clearly indicates the ferromagnetic behaviour of the film which is certainly due to the formation of ferromagnetic domains. The various magnetic parameters such as: remnant magnetization (Mr), coercivity (Hc) and the saturation magnetization (Ms) calculated using M-H loos were found 5.0×10^{-5} emu/cm³, 63.2 Oe and 6.4×10^{-4} emu/cm³, respectively. The saturation of the magnetization was determined by plotting M Vs 1/H (not



Fig. 5. M-H hysteresis loops for 5% Fe-CeO₂ TF. Inset shows the low filed M-H loop of 5% Fe-CeO₂ TF.

shown here). This value is in good agreement with some earlier reported results for doped CeO_2 [18].

Lee and his co-workers have reported a maximum saturation magnetization of 0.006 emu/g for 9% La doped CeO2 which decreased with increasing doping concentration [42]. Here, nearly same saturation has been obtained for 5% Fe dopant content. Yang et. al. have also reported a relatively large saturation of 1.12 μ_B /Mn as compared to other dopant ions [27]. Here in this work, with Fe dopant ions, $Ms = 6.4 \times$ 10^{-4} emu/cm³ has been obtained at a relatively lower dopant concentration as 5%, comprising $3.19 \times 10^{-6} \mu_B$ /Fe which is not very large but similar to some already reported work by Li et. al. [14]. Although these values are quite small as compared to 15.6 emu/cm³ as measured for Mn doped TiO₂ thin film [43], nonetheless, originate a weak room temperature ferromagnetism with a magnetic susceptibility of the order of 10^{-6} . Further, the temperature dependent behaviour of magnetization has been studied. Fig. 6 shows the magnetization vs temperature (M-T) and inverse susceptibility vs temperature (χ^{-1} - T) plot. The M-T curve was measured in the field cooled mode. In this process the sample was cooled in presence of 1000 Oe field and then the magnetization was recorded during heating up cycle. It can be seen from the M-T curve that the magnetization decreases with increase in temperature. The inverse susceptibility vs temperature curve was used to estimate the Curie temperature (T_C) of Fe-CeO₂ TF. In order to calculate the T_C, the higher temperature region of χ^{-1} - T plot was linearly fitted and then extrapolated on x-axis. It is found that Fe-CeO2 TF demonstrate the Curie temperature (T_C) \sim 300 K.

Since the undoped CeO₂ is a non-magnetic oxide, the value of magnetic moment points towards the role of magnetic dopant ions (Fe²⁺) into non-magnetic CeO₂. The spins of the unpaired electrons present in Fe - ions direct the spins of neighbouring ions, making the material ferromagnetic in nature. However, by comparing the magnetic moment due to Fe ions with that of total saturation, it can be stated here that the contribution of Fe ions to the total saturation magnetization of the material is very small. Therefore, there must be other elements which participate in enhancing ferromagnetism, excluding the Fe clusters or any other phases of iron that has been ruled out by XRD investigation. This directs us towards the formation of oxygen vacancies that has been confirmed from the analysis via XAS technique which evidences that in addition to the magnetic ${\rm Fe}^{2+}$ ions; oxygen vacancies and ${\rm Ce}^{3+}$ ions also contribute towards the alignment of spins in the local environment. The oxygen vacancies trap the electrons and form bound magnetic polarons causing alignment of the neighbouring spins. Thus, ferromagnetic assets of the compound may be associated with the formation of bound



Fig. 6. Magnetization vs temperature (M – T) and inverse susceptibility vs temperature ($1/\chi$ Vs T) plot of 5% Fe-CeO₂ TF.

magnetic polarons (BMPs) [44]. The ferromagnetic behaviour may also be attributed to the presence of mixed valence states of Fe^{2+}/Fe^{3+} ions as suggested by *Coey et. al.* [45] which have been found to be present in Fe-CeO₂ TF as determined by Fe $L_{3,2}$ NEXAFS analysis. Further, the Ce³⁺ ions accumulate near or at the surface, and the presence of Ce³⁺ ions on the surface enhances the hybridization between O 2p and Ce 4f for charge compensation and bring about the room temperature ferromagnetism in the film [14]. Therefore, this might be suggested here that in addition to Fe²⁺ ions, there are other factors such as oxygen vacancies, mixed valence states of Fe and reduced cerium that may be responsible for the room temperature ferromagnetism in Fe-CeO₂ TF. Further, the ferromagnetic behaviour has been found to increase with decreasing temperature from 300 K to 10 K which affirms that the increasing temperature destroys the ferromagnetism of the material.

4. Conclusions

We have successfully deposited Fe-CeO₂ TF on LAO (h00) substrate through PLD technique. XRD results confirmed the single-phase polycrystalline nature of the thin films with cubic fluorite structure along with preferred orientations. AFM micrographs clearly showed the effect of doping on the surface structures of the film. The roughness of the surface determined through analysis of AFM micrographs was found to be enhanced with Fe-doping. The structural analysis confirmed the well substitution of Fe²⁺ ions in place of Ce⁴⁺ host cation. The NEXAFS spectra revealed the mixed valence states (Fe²⁺/Fe³⁺) of Fe in doped thin film, while Ce remain to be in +4 oxidation state. M-H hysteresis loop validates the room-temperature ferromagnetic behaviour of pure and Fe-CeO₂ TF with T_c = ~300 K.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] R. Masrour, E.K. Hlil, Correlation of electronic structure and magnetic moment in Ga_{1-x} Mn_xN : first-principles, mean field and high temperature series expansions calculations, Physica A 456 (2016) 215–221, https://doi.org/10.1016/j. physa.2016.03.011.
- [2] R. Masrour, A. Jabar, A. Benyoussef, M. Hamedoun, Critical phenomena in Isingtype thin fi lms by Monte Carlo study, J. Magn. Magn Mater. 403 (2016) 167–171, https://doi.org/10.1016/j.jmmm.2015.11.083.
- [3] R. Masrour, A. Jabar, Surface behavior of magnetic phase transitions: Monte Carlo Study, Appl. Surf. Sci. 432 (2018) 78–84, https://doi.org/10.1016/j. apsusc.2017.08.063.
- [4] R. Masrour, A. Jabar, E.K. Hlil, M. Hamedoun, A. Benyoussef, A. Hourmatallah, A. Rezzouk, K. Bouslykhane, N. Benzakour, Spin and orbital magnetisms of NiFe Compound : density functional theory study and Monte Carlo simulation, Chin. Phys. Lett. 35 (2018), 036401, https://doi.org/10.1088/0256-307X/35/3/ 036401.
- [5] R. Masrour, A. Jabar, Size and diluted magnetic properties of diamond shaped graphene quantum dots : Monte Carlo study, Physica A 497 (2018) 211–217, https://doi.org/10.1016/j.physa.2017.12.141.
- [6] R. Masrour, E.K. Hlil, A. Jabr, M. Hamedoun, A. Benyoussef, A. Hourmatallah, K. Bouslykhane, N. Benzakour, A. Rezzouk, Magnetic and electronic properties of Mn2Sn thin films: first-principles calculations and high temperature series expansions, Chin. J. Phys. 56 (2018) 1985–1989, https://doi.org/10.1016/j. cjph.2018.08.023.
- [7] R. Masrour, A. Jabar, E ff ect of surface and bulk exchange interactions on superlattice materials with a mixed spins : a Monte Carlo study, Solid State Commun. 291 (2019) 15–20, https://doi.org/10.1016/j.ssc.2019.01.004.
- [8] R. Masrour, A. Jabar, E.K. Hlil, Modeling of the magnetocaloric e ff ect in Heusler Ni 2 MnGa alloy : Ab initio calculations and Monte Carlo simulations,

Intermetallics 91 (2017) 120–123, https://doi.org/10.1016/j. intermet.2017.08.012.

- [9] A. Jabar, R. Masrour, Effect of surface and interface couplings in thin film system: Monte Carlo simulation, Comput. Condens. Mater. 13 (2017) 91–95, https://doi. org/10.1016/j.cocom.2017.09.010.
- [10] A.S.E. Elyacoubi, R. Masrour, A. Jabar, Surface effects on the magnetocaloric properties of perovskites ferromagnetic thin films: a Monte Carlo study, Appl. Surf. Sci. 459 (2018) 537–543, https://doi.org/10.1016/j.apsusc.2018.08.020.
- [11] G. Kadim, R. Masrour, A. Jabar, Large magnetocaloric effect, magnetic and electronic properties in Ho 3 Pd 2 compound : Ab initio calculations and Monte Carlo simulations, J. Magn. Magn Mater. 499 (2020) 166263, https://doi.org/ 10.1016/j.jmmm.2019.166263.
- [12] R. Masrour, M. Hamedoun, A. Benyoussef, Magnetic phase transition in antiferromagnetic films, Phys. Lett. A. 373 (2009) 2071–2074, https://doi.org/ 10.1016/j.physleta.2009.04.003.
- [13] R. Masrour, M. Hamedoun, A. Benyoussef, Phase transition in Ising, XY and Heisenberg magnetic films, Appl. Surf. Sci. 258 (2012) 1902–1909, https://doi. org/10.1016/j.apsusc.2011.06.156.
- [14] M. Li, S. Ge, W. Qiao, L. Zhang, Y. Zuo, Relationship between the surface chemical states and magnetic properties of CeO₂ nanoparticles, Appl. Phys. Lett. 94 (2009) 152511, https://doi.org/10.1063/1.3079330.
- [15] M. Finazzi, L. Duò, F. Ciccacci, Magnetic properties of interfaces and multilayers based on thin antiferromagnetic oxide films, Surf. Sci. Rep. 64 (2009) 139–167, https://doi.org/10.1016/j.surfrep.2008.12.003.
- [16] R. Prakash, S. Kumar, C.G. Lee, S.K. Sharma, M. Knobel, J.I. Song, Study of Raman spectrum of Fe doped CeO₂ thin films grown by pulsed laser deposition, Adv. Mater. Res. 123–125 (2010) 375–378. https://doi.org/10.4028/www.scientific. net/AMR.123-125.375.
- [17] J. Qian, F. Chen, X. Zhao, Z. Chen, China rose petal as biotemplate to produce twodimensional ceria nanosheets, J. Nanoparticle Res. 13 (2011) 7149–7158, https:// doi.org/10.1007/s11051-011-0626-2.
- [18] C. Xia, C. Hu, P. Chen, B. Wan, X. He, Y. Tian, Magnetic properties and photoabsorption of the Mn-doped CeO₂ nanorods, Mater. Res. Bull. 45 (2010) 794–798, https://doi.org/10.1016/j.materresbull.2010.03.015.
- [19] C. Gopal Balaji, M. Melchor García, S. Lee Chul, Y. Shi, A. Shavorskiy, M. Matteo, G. Zixuan, S. Robert, B. Hendrik, A. Vojvodic, W.C. Chueh, Equilibrium oxygen storage capacity of ultrathin CeO_{2-d}, Nat. Commun. 8 (2017) 15360, https://doi. org/10.1038/ncomms15360.
- [20] S. Kumar, B.H. Koo, S.K. Sharma, M. Knobel, C.G. Lee, Influence of Co doping on structural, optical and magnetic studies of Co-doped CeO₂ nanoparticles, Nano. Br. Rep. Rev. 5 (2010) 349–355. https://doi.org/10.1142/S1793292010002268.
- [21] S. Kumar, Y.J. Kim, B.H. Koo, C.G. Lee, Structural and magnetic properties of Ni doped CeO₂ nanoparticles, J. Nanosci. Nanotechnol. 10 (2010) 7204–7207, https://doi.org/10.1166/jnn.2010.2751.
- [22] N.S. Ferreira, L.G. Abrac-ado, M.A. Maĉ, The effects of Cr-doping on the room temperature ferromagnetism of chemically synthesized CeO 2-d nanoparticles, Phys. B. 407 (2012) 3218–3221, https://doi.org/10.1016/j.physb.2011.12.069.
- [23] M.E. Khan, M.M. Khan, M.H. Cho, Ce³⁺-ion, surface oxygen vacancy, and visible light-induced photocatalytic dye degradation and photocapacitive performance of CeO₂-graphene nanostructures, Sci. Rep. 7 (2017) 5928, https://doi.org/10.1038/ s41598-017-06139-6.
- [24] D. Wang, Y. Kang, V. Doan-Nguyen, J. Chen, R. Küngas, N.L. Wieder, K. Bakhmutsky, R.J. Gorte, C.B. Murray, Synthesis and oxygen storage capacity of two-dimensional ceria nanocrystals, Angew. Chem. Int. Ed. 50 (2011) 4378–4381, https://doi.org/10.1002/anie.201101043.
- [25] D.M.D.M. Prabaharan, K. Sadaiyandi, M. Mahendran, S. Sagadevan, Structural, optical, morphological and dielectric properties of cerium oxide nanoparticles, Mater. Res. 19 (2016) 478–482, https://doi.org/10.1590/1980-5373-MR-2015-0698.
- [26] D.R. Mullins, The surface chemistry of cerium oxide, Surf. Sci. Rep. 70 (2015) 42–85, https://doi.org/10.1016/j.surfrep.2014.12.001.
- [27] S. Yang, Y. Zhang, Structural and magnetic studies of Mn-doped CeO₂ thin films prepared by sol-gel method, Integrated Ferroelectrics Int. J. 185 (2017) 176–182, https://doi.org/10.1080/10584587.2017.1369307.
- [28] R.N. Aljawfi, K. Kumari, A. Vij, M. Hashim, K.H. Chae, P.A. Alvi, S. Kumar, Tuning the surface morphology and local atomic structure of Mn – TiO 2 thin films using rapid thermal annealing, J. Mater. Sci. Mater. Electron. 29 (2018) 5982–5992, https://doi.org/10.1007/s10854-018-8572-8.
- [29] S. Kumar, S. Gautam, T.K. Song, K.H. Chae, K.W. Jang, S.S. Kim, Electronic structure study of Co doped CeO₂ nanoparticles using X-ray absorption fine structure spectroscopy, J. Alloys Compd. 611 (2014) 329–334, https://doi.org/ 10.1016/j.jallcom.2014.05.025.
- [30] S. Naseem, I.V. Pinchuk, Y. Kelly, R.K. Kawakami, S. Khan, S. Husain, W. Khan, Epitaxial growth of cobalt doped TiO₂ thin films on LaAlO₃ (100) substrate by molecular beam epitaxy and their opto-magnetic based applications, Appl. Surf. Sci. 493 (2019) 691–702, https://doi.org/10.1016/j.apsusc.2019.07.017.
- [31] M.S. Anwar, S. Kumar, N. Arshi, F. Ahmed, Y.J. Seo, C.G. Lee, B.H. Koo, Structural and optical study of samarium doped cerium oxide thin films prepared by electron beam evaporation, J. Alloys Compd. 509 (2011) 4525–4529, https://doi.org/ 10.1016/j.jallcom.2011.01.067.
- [32] Y. Zhang, F. Feng, K. Shi, H. Lu, S. Xiao, W. Wu, R. Huang, T. Qu, X. Wang, Z. Wang, Z. Han, Surface morphology evolution of CeO₂/YSZ (001) buffer layers fabricated via magnetron sputtering, Appl. Surf. Sci. 284 (2013) 150–154, https:// doi.org/10.1016/j.apsusc.2013.07.072.

- [33] V. Trtík, R. Aguiar, F. Sánchez, C. Ferrater, M. Varela, Study of the epitaxial growth of CeO₂(0 0 1) on yttria-stabilized zirconia/Si(0 0 1), J. Cryst. Growth 192 (1998) 175–184, https://doi.org/10.1016/S0022-0248(98)00445-X.
- [34] V. Kumar, H. Sharma, S.K. Singh, S. Kumar, A. Vij, Enhanced near-band edge emission in pulsed laser deposited ZnO/c-sapphire nanocrystalline thin films, Appl. Phys. Mater. Sci. Process 125 (2019), https://doi.org/10.1007/s00339-019-2485-0, 0.
- [35] H.K. Webb, V.K. Truong, J. Hasan, C. Fluke, R.J. Crawford, E.P. Ivanova, Roughness parameters for standard description of surface nanoarchitecture, Scanning 34 (2012) 257–263, https://doi.org/10.1002/sca.21002.
- [36] G.J. Colpas, M.J. Maroney, C. Bagyinka, M. Kumar, W.S. Willis, S.L. Suib, N. Baidya, P.K. Mascharak, X-ray spectroscopic studies of nickel complexes, with application to the structure of nickel sites in hydrogenases, Inorg. Chem. 30 (1991) 920–928.
- [37] S. Gautam, S. Kumar, P. Thakur, K.H. Chae, R. Kumar, B.H. Koo, C.G. Lee, Electronic structure studies of Fe-doped ZnO nanorods by x-ray absorption fine structure, J. Phys. D Appl. Phys. 42 (2009) 175406, https://doi.org/10.1088/ 0022-3727/42/17/175406.
- [38] S. Kumar, Y.J. Kim, B.H. Koo, S.K. Sharma, J.M. Vargas, M. Knobel, S. Gautam, K. H. Chae, D.K. Kim, Y.K. Kim, C.G. Lee, Structural and magnetic properties of chemically synthesized Fe doped ZnO, J. Appl. Phys. 105 (2009), 07C520, https:// doi.org/10.1063/1.3073933.
- [39] E.C. Rodrigues, S.K. Sharma, A.S. de Menezes, K.H. Chae, S. Gautam, R.N. Aljawf, S. Kumar, Rapid thermal annealing induced modification in structural and electronic structure properties of Ti_{0.95}Co_{0.05}O_{2-δ} thin films, Mater. Res. Bull. (2016), https://doi.org/10.1016/j.materresbull.2016.06.038.

- [40] W.-C. Wang, S.-Y. Chen, P.-A. Glans, J. Guo, R.-J. Chen, K.-W. Fong, C.-L. Chen, A. Gloter, C.-L. Chang, T.-S. Chan, J.-M. Chen, J.-F. Lee, C.-L. Dong, Towards understanding the electronic structure of Fe-doped CeO₂ nanoparticles with X-ray spectroscopy, Phys. Chem. Chem. Phys. 15 (2013) 14701, https://doi.org/ 10.1039/c3cp52054d.
- [41] S. Kumar, J.S. Park, D.J. Kim, M.H. Lee, T.K. Song, S. Gautam, K.H. Chae, S.S. Kim, M.H. Kim, Electronic structure and magnetic properties of Co doped TiO₂ thin films using X-ray absorption spectroscopy, Ceram. Int. 41 (2015) S370–S375, https:// doi.org/10.1016/j.ceramint.2015.03.209.
- [42] W. Lee, S. Chen, E.N. Tseng, A. Gloter, C.L. Chen, A study of defect structure in ferromagnetic nanocrystalline CeO2 : effect of ionic radius, J. Phys. Chem. C 120 (2016) 14874–14882, https://doi.org/10.1021/acs.jpcc.6b02817.
- [43] S. Kumar, S. Gautam, G.W. Kim, F. Ahmed, M.S. Anwar, K.H. Chae, H.K. Choi, H. Chung, B.H. Koo, Structural, magnetic and electronic structure studies of Mn doped TiO2thin films, Appl. Surf. Sci. 257 (2011) 10557–10561, https://doi.org/ 10.1016/j.apsusc.2011.07.050.
- [44] K. Kumari, R. Naji, Y.S. Katharria, S. Dwivedi, K.H. Chae, R. Kumar, A. Alshoaibi, P.A. Alvi, S. Dalela, S. Kumar, Study the contribution of surface defects on the structural, electronic structural, magnetic, and photocatalyst properties of Fe : CeO₂ nanoparticles, J. Electron. Spectrosc. Relat. Phenom. 235 (2019) 29–39, https://doi.org/10.1016/j.elspec.2019.06.004.
- [45] J.M.D. Coey, M. Venkatesan, C.B. Fitzgerald, Donor impurity band exchange in dilute ferromagnetic oxides, Nat. Mater. 4 (2005) 173–179, https://doi.org/ 10.1038/nmat1310.