A study of structural, optical and ferromagnetic properties of sol-gel derived Cr and Fe co-doped CeO₂ nanoparticles

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Abstract

The Cr and Fe co-doped CeO₂ nanoparticles (Ce_{0.98-x}Cr_xFe_{0.02}O₂: where $x = 0, 0.01, 0.02, 0.03$) were prepared by sol-gel method. Effects of additional Cr dopant on structural, optical and magnetic properties of Fe doped CeO₂ nanoparticles have been investigated by X-ray diffraction (XRD), optical absorption spectra, Raman spectroscopy (Raman) and physical property measurement system (PPMS). XRD and Raman studied showed that all samples are single-phase of CeO₂ original cubic fluorite crystal structure, Cr can readily be incorporated into the lattice of Fe doped CeO₂ and no ferromagnetic secondary phase was found. With the increase of Cr doping concentration, the grain size and crystal quality decreases. The values of optical bandgap energy extracted from the absorption coefficient increase with the increase of Cr doping concentration. The PPMS studied show hysteresis phenomenon, which indicates that the samples have ferromagnetic properties at 300 K. With the increase of Cr content, the saturation magnetization increase obviously. Based on the results of XRD and Raman, it can be concluded that the ferromagnetism is the intrinsic property of the sample.

1. Introduction

Diluted magnetic oxide semiconductors (DMOS) have great potential applications in spintronic devices because of their optical, electrical and magnetic properties [1–3]. Transition metal doped CeO₂ is one of the most promising and widely studied DMOS systems [2–5]. However, there is a heated debate on the origin of ferromagnetic properties of these DMOS systems. CeO₂ belongs to fluorite structure in cubic system. The coordination number of oxygen is four and that of cerium is eight. CeO₂ can be converted into nonstoichiometric CeO_{2-δ} at high temperature, and the deviation δ is $0 < \delta < 0.5$ [6]. Nonstoichiometric CeO_{2-δ} can also maintain a fluorite crystal structure well under the condition of V_O formed by anoxia. Therefore, CeO₂ has a good ability to store and release oxygen and is easy to manipulate V_O defects. The unique physical and chemical properties of CeO₂ make it widely used in the fields of luminescence, polishing, UV absorption, automobile exhaust purification, solid oxide fuel cell, optical coating and oxygen sensor. CeO₂ based DMOS has also attracted great attention. The main reasons for these are its structural properties that are similar to silicon [7]. Therefore, CeO₂ is considered as a potential substitute for silicon semiconductor. In addition, CeO₂ has better visible light transmittance, which makes it possible to develop new transparent spintronic devices. A large number of studies have shown that CeO₂ doped with metal or transition metal exhibits good room temperature ferromagnetism [2–10]. However, the origin of ferromagnetism in CeO₂ based DMOS system is still controversial. Some studies have found that doping 3d transition metals can provide local magnetism, and the defect in CeO₂ matrix can provide charge, ferromagnetic properties are obtained by s-p-d electron exchange [9, 10]. Other studies suggest that ferromagnetism originates from defects in CeO₂ matrix, because ferromagnetism is also observed in undoped CeO₂ and rare earth (such as Nd, Sm or Pr) doped CeO₂ [11–13]. In most studies, V_O is considered to be an important reason for room temperature ferromagnetism in CeO₂ based DMOS systems. A large amount of V_O can be formed in the anoxic CeO₂ matrix. The magnetic exchange

coupling induced by V_O leads to room temperature ferromagnetism. In view of the current reported in the literature, how to control the various properties of CeO_2 based DMOS system and clarify the related magnetic and transport properties due to the local structure of doped ions and spin are the difficulties in the current research. Therefore, it is necessary to further study the preparation and properties of different elements doped CeO_2 based DMOS.

There are many methods for preparing different elements doped CeO_2 based DMOS nanoparticles, such as sol-gel, thermal decomposition, hydrothermal, microemulsion and ball milling methods [2–13]. In these methods, sol-gel method is more attractive because of its simple equipment, convenient operation, low cost, low sintering temperature and easy control of chemical components. The mild and adjustable reaction conditions are conducive to the synthesis of different elements doped CeO_2 based DMOS nanoparticles. In this paper, Cr is chosen as additional dopants for Fe doped CeO_2 DMOS systems. The Cr and Fe co-doped CeO_2 nanoparticles ($\text{Ce}_{0.98-x}\text{Cr}_x\text{Fe}_{0.02}\text{O}_2$: where $x = 0, 0.01, 0.02, 0.03$) were synthesized by sol-gel technique. The effects of Cr doping concentration on the structure, optical and ferromagnetic properties of 2% Fe doped CeO_2 based DMOS were investigated by X-ray diffraction, Raman spectroscopy, optical absorption spectra and physical property measurement system (PPMS). The source of room temperature ferromagnetism (RTFM) in Cr-Fe co-doped CeO_2 based DMOS nanoparticles has been discussed.

2. Experiments

Additional Cr dopant of 2% Fe doped CeO_2 based DMOS nanoparticles ($\text{Ce}_{0.98-x}\text{Cr}_x\text{Fe}_{0.02}\text{O}_2$: where $x = 0, 0.01, 0.02, 0.03$) were prepared by sol-gel method. The preparation process is as follows. Stoichiometric amount of Ce (III) nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), chromium nitrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and ferric Nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) was used as solutes to obtain desired compositions. 2-methoxyethanol ($\text{C}_3\text{H}_8\text{O}_2$) was used as solvent and acetylacetone ($\text{CH}_3\text{COCH}_2\text{COCH}_3$) was used as stabilizer. These solutes were completely dissolved in 2-methoxyethanol with stirring for 1 h at 65 °C, then the stabilizer acetylacetone was added, and finally stirred for 3 h at room temperature. In order to study the effect of Cr doping on the structural, optical and magnetic properties of 2% Fe doped CeO_2 based DMOS, here we kept Fe doping concentration as a constant of 2 at.% with the variation of Cr doping content from 0 to 3 at.%. Cr doping was achieved by the introduction of appropriate amount of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. These prepared precursor solutions were put in a furnace for 24 h at 100°C to eliminate excess water and form the xerogel. Then, the xerogel was calcined at 800°C for 2 h to eliminate organic materials, and finally $\text{Ce}_{0.98-x}\text{Cr}_x\text{Fe}_{0.02}\text{O}_2$ nanoparticles were prepared.

The crystal structure of $\text{Ce}_{0.98-x}\text{Cr}_x\text{Fe}_{0.02}\text{O}_2$ nanoparticles were characterized by using RIGAKU D-MAX 2200 VPC X-ray diffractometer (XRD) equipped with a Cu-K α ($\lambda = 1.54 \text{ \AA}$) source. The room temperature Raman spectroscopy of these nanoparticles was measured by using Confocal Micro-Raman Spectrometer (inVia Reflex, Renishaw) with 514 nm excitation source under air ambient condition. Optical

absorption spectra were measured in a band ranging from the ultraviolet to visible regions (UV-Vis) by using a UV-3150 SHIMADZU. Magnetic measurements as a function of temperature ($M \sim T$) at $H = 1000$ Oe in the temperature range from 10 to 300 K and magnetization curves as a function of magnetic field ranging $-100 < H < 100$ kOe ($M \sim H$) measured at $T = 300$ K were done by commercial physical property measurement system (PPMS, quantum design, model 6000). In Table 1, some properties of $\text{Ce}_{0.98-x}\text{Cr}_x\text{Fe}_{0.02}\text{O}_2$ (where $x = 0, 0.01, 0.02$ and 0.03) nanoparticles, such as particle size (D), optical band gap energy (E_g), saturation moment (M_s), and coercivity (H_c) are given.

Table 1
Some properties of $\text{Ce}_{0.98-x}\text{Cr}_x\text{Fe}_{0.02}\text{O}_2$
nanoparticles: particle size (D), optical band gap
energy (E_g), saturation moment (M_s), and
coercivity (H_c)

Cr content x	D (nm)	E_g (eV)	M_s (em μ /g)	H_c (Oe)
0.00	24.8	3.21	0.036	36.42
0.01	17.2	3.24	0.051	39.33
0.03	13.4	3.27	0.082	41.58
0.05	10.9	3.33	0.118	61.82

3. Results And Discussion

Fig. 1 shows the XRD patterns for $\text{Ce}_{0.98-x}\text{Cr}_x\text{Fe}_{0.02}\text{O}_2$ (where $x = 0, 0.01, 0.02, 0.03$) nanoparticle samples taken at room temperature. The XRD patterns show that all the samples have sharp peaks, which indicating that the samples have good crystallinity, and the crystal orientation does not depend on the Cr content. The obtained XRD patterns are consistent with the XRD diffraction data of CeO_2 powder given in JCPDF 34-0394, which indicates that the samples prepared in this experiment belong to Fm-3m space group and have cubic fluorite crystal structure of pure CeO_2 . Within the XRD detection limit, no additional diffraction peak related to the second phases of Cr or Fe were observed, which confirms the complete solubility of Cr and Fe ions in the ceria crystal structure. This indicates that Cr and Fe substituted for Ce in CeO_2 host without changing the fluorite crystal structure. From Fig. 1, it is also seen that the intensity of diffraction peak decreases as the increase of Cr doping concentration. This indicates that the quality of crystallization is deteriorated. All diffraction peaks are broadened as the Cr content increase, which indicated the fine nature of the small particles. By using Debye Scherrer formalism , where β is the full-width at half-maximum in radians, is the Bragg's angle in degrees, and λ is the wavelength of X-rays (1.54 Å for Cu-K α), the average grain size of $\text{Ce}_{0.98-x}\text{Cr}_x\text{Fe}_{0.02}\text{O}_2$ powders has been determined from the peak (111) broadening in the XRD patterns. The calculated grain size was 24.8, 17.2, 13.4 and 10.9 nm for x values of 0, 0.01, 0.02, and 0.03, respectively. The grain size decreases with the increase of the amount of Cr (see Table 1). The radii of Cr and Fe ions are about 0.73 Å and 0.61 Å, respectively. The radii of Ce ions in CeO_2 are 0.97 Å. The radii of Cr or Fe ions are smaller than those of Ce ions. If substitution

doping occurs, the grain size will decrease, which is consistent with the results of XRD. On the other hand, as the Cr content increases, the diffraction peak shifts to a large angle. This indicates the lattice constant of the sample decrease gradually. The reason why additional Cr dopant affects the structure of Fe doped CeO₂ nanoparticles is that Cr will inhibit the crystallization of the samples. When Cr or Fe ions replace Ce ions, V_O will be produced due to different valence states, and different ion radii will lead to lattice distortion or other defects. V_O and lattice distortion or other defects will increase with the increase of Cr doping concentration.

The structure of Ce_{0.98-x}Cr_xFe_{0.02}O₂ nanoparticles was further studied by Raman spectroscopy. Fig. 2 shows the room temperature Raman spectra of Ce_{0.98-x}Cr_xFe_{0.02}O₂ nanoparticles under 514 nm excitation light. There are two obvious peaks in the Raman spectra of the samples. The most obvious one is the one at 462.5 cm⁻¹. In addition, for Cr doped samples, a weak peak related to V_O absorption was observed at 545 cm⁻¹ [14]. We have not observed any Raman vibration peaks of Cr or Fe related oxides. This indicates that there is no secondary phase related to Cr or Fe in Cr-Fe co-doped CeO₂ nanoparticles. The doping of Cr and Fe takes the place of Ce lattice position in CeO₂ host. Raman study further confirmed the XRD results. The strong band (at 462.5 cm⁻¹) belongs to the lattice mode (F_{2g}) of CeO₂ cubic fluorite structure. It related to a first-order symmetrical stretching mode of the Ce-O₈ vibrational unit. This Raman peak (at 462.5 cm⁻¹) changes with the crystal structure (such as defects, Vo, grain size, etc.). Generally, the strength of the peak is related to the grain size. The larger the grain size, the stronger the peak strength. The shift of the peak position is also related to the grain size. The peak moves to the lower wavenumber as the grain size decreases. Raman studies show that Ce_{0.98-x}Cr_xFe_{0.02}O₂ nanoparticles have the same structure as pure cubic CeO₂. With the increase of Cr doping concentration, the peak position (at 462.5 cm⁻¹) remains unchanged, but the intensity decreases. This result show that additional Cr doping affects the structural modification (such as the change of the grain size, crystal quality and defects) of Fe doped CeO₂ nanoparticles. A weak Raman vibration peak at 545 cm⁻¹ was observed for additional Cr doping samples. This Raman vibration peak related to Vo absorption [14], which indicates Vo was generated due to charge compensation in the additional Cr doping samples. The Raman results show additional Cr doping can increase Vo and other types of crystal defects in the samples. Combined with XRD and Raman spectra, we can conclude that Ce_{0.98-x}Cr_xFe_{0.02}O₂ nanoparticles have polycrystalline structure, which is the same as that of pure cubic phase of CeO₂. The samples have Vo and other types of crystal defects. With the increase of Cr doping concentration, the grain size decreases, and the Vo and other types of crystal defects increase.

The optical absorption measurement can investigate the behavior of semiconductor nanostructure. The optical bandgap energy (E_g) can be modified by particle size due to the effect of quantum confinement. The UV-Vis absorption spectra of Ce_{0.98-x}Cr_xFe_{0.02}O₂ (where x = 0, 0.01, 0.02 and 0.03) nanoparticles are presented in Fig.3. All samples show strong absorption below 400 nm (3.10 eV). The abrupt reduction in

the absorption curves is equivalent to the electronic excitation of electrons passing through the energy gap from the valence band. In order to extract the E_g values, first the Tauc plots which are the plots of $(\alpha hu)^2$ vs photon energy hu were achieved. These are shown on Fig. 4. Then, according to the Tauc equation $(\alpha hu)^2 = A(hu - E_g)$, here, α is the optical absorption coefficient, hu is the photon energy. A is a constant, and E_g is the optical bandgap energy, the E_g values can be extracted by the linear extrapolation of the linear portion of the Tauc plots [15]. As shown in Fig. 4, by extrapolating the linear part of the Tauc plot to $(\alpha hu)^2 = 0$, the E_g values of $\text{Ce}_{0.98-x}\text{Cr}_x\text{Fe}_{0.02}\text{O}_2$ nanoparticles are 3.21, 3.24, 3.27 and 3.33 eV for $x = 0, 0.01, 0.02$ and 0.03 , respectively (see Table 1). With increasing of Cr doping content, the E_g value increases slightly. Accordingly, the analysis of the UV-Vis spectra approves the reduction of the particle size detected from XRD investigations and proposes the increasing of E_g value with increasing the Cr content into CeO_2 semiconducting nanoparticles. Hence, the observed increase of the E_g value of additional Cr doping Fe-doped CeO_2 nanoparticles is due to the decrease in the particle size of the samples with Cr content that attributed to a strong quantum confinement. Similar result was reported for Cr doped ZnO nanoparticles [16]. The surface and interface effects are the other reason for the increasing E_g value with increasing of Cr doping content. Larger particles show enlarged scattering which produces broaden and shift for the absorption peak towards longer wavelengths due to larger optical cross sections. However, for small particles, the absorption peak is damped due to the reduced mean free path of the electrons. The E_g values in this experiment are lower than that reported in literature. For example, Chen et.al. reported that the E_g value of CeO_2 nanoparticles synthesized by precipitation method ranged from 3.56 to 3.71 eV [17]. Maensiri et.al. reported that the E_g value of CeO_2 nanoparticles synthesized by sol-gel method ranged from 3.57 to 3.61 eV [18]. This may be due to the Vo in the $\text{Ce}_{0.98-x}\text{Cr}_x\text{Fe}_{0.02}\text{O}_2$ nanoparticles. According to the results of XRD and Raman, Vo may be generated in $\text{Ce}_{0.98-x}\text{Cr}_x\text{Fe}_{0.02}\text{O}_2$ nanoparticles due to the charge compensation effect. The Vo at the interface between grains will change the electronic structure of CeO_2 and narrow the band gap, resulting in the red shift of absorption band edge. Similar results have been reported in other systems [19-21]. In addition, Paula et. al. reported that the E_g value of CeO_2 nanoparticles was 3.26 eV [22]. This value is very close to the E_g value (3.2 eV) of n-type semiconductor CeO_2 , and is also close to the value obtained in this experiment.

Fig. 5 shows the temperature dependence of the magnetization (M vs T) of the $\text{Ce}_{0.98-x}\text{Cr}_x\text{Fe}_{0.02}\text{O}_2$ (where $x = 0$, and 0.02) nanoparticles under the field-cooled (FC) mode at $H = 1000$ Oe in the range from 10 to 300 K. The magnetization M shows a slight increase from 300 to 50 K, followed by a steep increase below 50 K until the lowest temperature of 10 K in this measurement is reached. Ferromagnetic (FM) ordering for the $\text{Ce}_{0.98-x}\text{Cr}_x\text{Fe}_{0.02}\text{O}_2$ (where $x = 0$, and 0.02) nanoparticles was clearly observed in the temperature range from 10 to 300 K. The Curie temperature of the samples is above 300 K. In addition, the magnetization of $\text{Ce}_{0.96}\text{Cr}_{0.02}\text{Fe}_{0.02}\text{O}_2$ sample is larger than that of $\text{Ce}_{0.98}\text{Fe}_{0.02}\text{O}_2$ sample in the whole measured temperature range. These imply that additional Cr dopant can improve the ferromagnetism of Fe-doping CeO_2 nanoparticles.

Fig. 6 shows the hysteresis loops (M - H curves) of $\text{Ce}_{0.98-x}\text{Cr}_x\text{Fe}_{0.02}\text{O}_2$ (where $x=0, 0.01, 0.02$ and 0.03) nanoparticles measured at 300 K. As shown in Fig. 6, the samples with different Cr doping concentrations exhibit FM properties at 300 K. The saturation magnetization (M_s) of $\text{Ce}_{0.98-x}\text{Cr}_x\text{Fe}_{0.02}\text{O}_2$ nanoparticles are 0.036, 0.051, 0.082 and 0.118 emu/g for x is 0, 0.01, 0.02 and 0.03, respectively. The saturation magnetization increases with the increase of the additional Cr doping concentration (see Table 1). The coercive field (H_C) values calculated from hysteresis loops were in the range from 36 to 62 Oe for different Cr concentration (also shown in Table 1). The hysteresis loops have small coercive field and low remanence featured a soft ferromagnetism. This observation is in agreement with the reported data [2-13].

The possible reasons for the ferromagnetism of $\text{Ce}_{0.98-x}\text{Cr}_x\text{Fe}_{0.02}\text{O}_2$ (where $x=0, 0.01, 0.02$ and 0.03) nanoparticles are Cr or Fe clusters, defects or V_O , and FM exchange coupling. Based on the results of XRD and Raman spectroscopy, we believe that the first case is impossible because no Cr or Fe clusters are detected in $\text{Ce}_{0.98-x}\text{Cr}_x\text{Fe}_{0.02}\text{O}_2$ nanoparticles. According to the charge compensation effect, when Cr^{2+} / Cr^{3+} replaces the lattice position of Ce^{4+} , V_O will be produced due to the difference of valence state. Meanwhile, the lattice distortion or defect will be produced due to the difference of ionic radius. Defects or V_O may be responsible for the ferromagnetism of these samples [23]. On the basis of F-center mediated ferromagnetic coupling mechanism (FCE) used in insulated DMO [24-27], more V_O will provide more coupling centers thus induce larger M_s . The increase in Cr doping concentration favored FM interactions because most of the V_O are formed. Therefore, the M_s is enhanced with additional Cr dopant. Defects have also been reported as one of the possible reason for the FM origination [28]. The V_O or defects increases as increasing the additional Cr dopant concentration. Basing on the FM mechanism of the defects/ V_O through the FCE interaction, it is readily to expect that the ferromagnetism increases by additional Cr dopant increasing. In the case of FM exchange coupling, the structure of Cr-O-Cr structure can produce ferromagnetism by p-d superexchange. Similarly, with additional Cr dopant content increasing, the amount of Cr-O-Cr structure increase, so the ferromagnetism of the samples increases with the increase of Cr doping amount. However, due to the small amount of Cr dopant in the sample, the ferromagnetism produced by this interaction is weaker than that produced by FCE interaction. Therefore, it can be considered that the ferromagnetism observed in $\text{Ce}_{0.98-x}\text{Cr}_x\text{Fe}_{0.02}\text{O}_2$ nanoparticles is mainly caused by FCE interaction. This ferromagnetism is intrinsic.

4. Conclusions

In summary, $\text{Ce}_{0.98-x}\text{Cr}_x\text{Fe}_{0.02}\text{O}_2$ (where $x=0, 0.01, 0.02$ and 0.03) nanoparticles were successfully prepared by sol-gel method. The results of XRD show a cubic structure (Fm-3m space group) and particle average sizes varying from 24.8 to 10.9 nm. Raman results are in good accordance with XRD data. Within the XRD and Raman detection limit, no secondary phase related to Cr and Fe is found, and $\text{Ce}_{0.98-x}\text{Cr}_x\text{Fe}_{0.02}\text{O}_2$ nanoparticles have the same structure of pure CeO_2 . The optical absorption spectra of the nanoparticles show strong absorption below 400 nm (3.10 eV). The bandgap energy was found to

increase slightly from 3.21 eV ($x = 0$) to 3.33 eV ($x = 0.03$) with increasing the additional Cr doping level which is related to the quantum confinement effect. Room temperature ferromagnetism is observed for $\text{Ce}_{0.98-x}\text{Cr}_x\text{Fe}_{0.02}\text{O}_2$ nanoparticles. The saturated magnetization (M_s) increased with increasing the additional Cr content. The FM behavior can be attributed to the presence of dopant ions mediated by Vo. These results suggested that additional Cr dopant can enhance the FM of Fe-doped CeO_2 , and $\text{Ce}_{0.98-x}\text{Cr}_x\text{Fe}_{0.02}\text{O}_2$ nanoparticles are good candidate for designing optoelectronic and spintronic devices.

Declarations

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Figures

Figure 1

The XRD patterns of the $\text{Ce}_{0.98-x}\text{Cr}_x\text{Fe}_{0.02}\text{O}_2$ (where $x = 0, 0.01, 0.02$ and 0.03) nanoparticles

Figure 2

Raman spectra of the $\text{Ce}_{0.98-x}\text{Cr}_x\text{Fe}_{0.02}\text{O}_2$ (where $x = 0, 0.01, 0.02$ and 0.03) nanoparticles

Figure 3

Optical absorption spectra of the $\text{Ce}_{0.98-x}\text{Cr}_x\text{Fe}_{0.02}\text{O}_2$ (where $x = 0, 0.01, 0.02$ and 0.03) nanoparticles measured at room temperatures

Figure 4

Curves of $(\alpha h\nu)^2$ vs photon energy $h\nu$ of the Ce_{0.98-x}Cr_xFe_{0.02}O₂ (where $x = 0, 0.01, 0.02$ and 0.03) nanoparticles

Figure 5

Magnetization curves as a function of temperature (M vs T) with applied field $H=1000$ Oe of the $\text{Ce}_{0.98-x}\text{Cr}_x\text{Fe}_{0.02}\text{O}_2$ (where $x = 0$, and 0.02) nanoparticles

Figure 6

M (H) measurements at 300 K of the $\text{Ce}_{0.98-x}\text{Cr}_x\text{Fe}_{0.02}\text{O}_2$ (where $x = 0, 0.01, 0.02$ and 0.03) nanoparticles