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Absence of room temperature ferromagnetism in Fe stabilized ZrO_2 nanostructures and effect of Fe doping on its structural, optical and luminescence properties

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ABSTRACT

Undoped and Fe doped ZrO_2 nanostructures were synthesized using sol–gel method. The structural analysis revealed that the tetragonal phase of ZrO_2 nanostructures can be stabilized at 700 °C by 10 at.% doping of Fe into ZrO_2 matrix for particle size less than 10 nm. The value of optical band gap of Fe doped ZrO_2 nanostructures is decreased with Fe doping. It could be due to many-body interaction between Zr and Fe. The presence of oxygen vacancies in the synthesized samples was confirmed by PL measurements. VSM measurements revealed the room temperature ferromagnetism (RTFM) in undoped ZrO_2 nanostructures. However, the RTFM of the material goes off by Fe doping into ZrO_2 matrix. The Fe doping induces magnetic transition from ferromagnetic to paramagnetic in Fe doped tetragonal ZrO_2 nanostructures. The paramagnetic nature of Fe doped ZrO_2 nanostructures is explained by density functional theory (DFT) employing breaking symmetry approach (BS). The theoretical results show that the antiferromagnetic interaction between Zr–Fe and Fe–Fe may be responsible for the paramagnetic nature of Fe doped ZrO_2 nanostructures.

1. Introduction

ZrO_2 (Zirconia) is a wide band gap metal oxide having promising applications in various fields of science and technology [1,2]. The wide band gap of ZrO_2 nanostructures can be lowered by the doping of suitable cations like Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}. The doping of transition metal cations can facilitate the development of new physical and chemical properties of ZrO_2 nanostructures [3]. In general, ZrO_2 exists in three crystalline phases, monoclinic (m), tetragonal (t) and cubic (c). Among these crystalline phases of ZrO_2, the desired crystal phase of ZrO_2 can be obtained by thermal treatment [4]. By doping of transition metal such as; Mn, Fe, Co, Ni in a certain amount, any of these crystalline phases of ZrO_2 can be stabilized at lower temperature [5]. The appropriate doping of these transition materials into ZrO_2 matrix may induce the ferromagnetic properties at room temperature which can be used as dilute magnetic semiconductor (DMS). Recently, metal oxide based DMS materials have attracted considerable attention of research community because of its multifunctional properties such as; wide band gap, high n-type carrier concentration, ecological safety, durability, low cost and capability to be grown at low temperature. These oxide based DMS materials can find application in making spintronic devices. Basically, spintronics is new active area of research where spin and charge of electron have been used to control the function of electronics devices. Spin based electronic devices have numerous advantages over the conventional charge-based devices such as nonvolatility, higher integration densities, data-processing speed, etc. Recently, the effect of Fe doping on ferromagnetic properties of metal oxides have widely been studied by the different research group [6–9]. Ostanin et al. [6] have reported that the Fe or Mn stabilized cubic ZrO_2 nanostructures has ferromagnetic nature above 500 K and it may be used as spintronics material. Nomura et al. [7] have reported the magnetic behaviour of $Sn_{1-x}Fe_xO_2$ nanostructures synthesized by sol–gel method. In the study, they have shown that the ferromagnetism is not originated due to Fe doping but it could be originated due to presence of defects in the material. Patel et al. [8] reported had RTFM in Fe doped TiO_2 nanorods. The RTFM in TiO_2 nanostructures is attributed to the F-center induced exchange mechanism (FCE), commonly known as bound magnetic polaron

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(BMP). Hong et al. [9] had found RTFM in Fe doped HfO_2 thin films. They also have shown that the Fe doping was not the main cause for origin of RTFM in HfO_2 thin films but doped Fe acts as a catalyst that induced oxygen vacancies in the HfO_2 matrix which caused RTFM in HfO_2 thin films. Karmakar et al. [10] have studied the ferromagnetism in Fe doped ZnO nanocrystals. They have reported that the RTFM is promoted in Fe doped ZnO nanostructures due to Zn vacancies.

The effect of Fe doping on physicochemical, magnetic and optical properties of ZrO_2 nanostructures have also been studied widely by different research group [3,11–15]. Sangalli et al. [13] have explored the magnetic properties of Fe doped ZrO_2 nanostructures by performing both, theoretical and experimental studies. They have explained the presence of RTFM in Fe doped ZrO_2 nanostructures in terms of impurity band model and standard super-exchange mechanism. Yu et al. [14] have predicted the absence of RTFM in Fe doped ZrO_2 nanostructures and explained the RTFM in terms of excess of oxygen vacancies in Fe stabilized ZrO_2 nanostructures. In view of above discussed studies on ZrO_2 and transition metal doped ZrO_2 nanostructures, the origin of RTFM in Fe doped ZrO_2 nanostructures has not been addressed yet properly and therefore the origin of RTFM in transition metal doped ZrO_2 nanostructures is still open for the material scientists.

Thus, in this study, we presented a systematic report on effect of Fe doping on structural, optical and magnetic properties of ZrO_2 nanostructures synthesized by sol–gel method. In the study, we have mainly focused on optical and magnetic properties of Fe doped ZrO_2 nanostructures since most of the reported studies are done on ZrO_2 thin film. The experimentally observed magnetic properties are further explained by calculating spin exchange interaction constant (J) employing breaking symmetry (BS) approach using density functional theory (DFT) calculations.

2. Experimental section

2.1. Synthesis of undoped and Fe doped ZrO_2 nanostructures

A facile sol–gel method was used to synthesize ultrafine powder of undoped and Fe doped ZrO_2 nanostructures. The steps used in synthesis process are shown in Fig. 1. The synthesis of undoped and Fe doped ZrO_2 nanostructures was done using $ZrOCl_2.8H_2O$ (SRL Pvt. Ltd., India) and $Fe(NO_3)_3.8H_2O$ (Panreac) precursors without further purification. The appropriate amount of $ZrOCl_2.8H_2O$ was dissolved in 50 ml of distilled water to make 0.5 M aqueous solution and then appropriate amount of $Fe(NO_3)_3.8H_2O$ was dissolved in the mix solution. The resultant solution was stirred vigorously for one hour. The ammonia solution (Merck, 25 wt %) was added into the final solution drop wise during the stirring until the pH value of solution was reached to the range of 10–12. After adding ammonia to the above prepared solution, a white colour precipitate was formed. The solution was kept on stirring on room temperature till the gel type nature of final solution was formed. Thereafter, the gel solution was dried at ~100 °C and then grinded to obtain the resulting powder. The powder form of the sample was then calcined at 400 °C for 3 h to obtain the final product. The undoped ZrO_2 sample was also prepared by following the same procedure without adding Fe precursor. The undoped ZrO_2 sample calcined at 400 °C was named as ZP4. The Fe doped (1, 3, 5, 7 and 10 at. %) ZrO_2 powder samples calcined at 400 °C were marked as ZF14, ZF34, ZF54, ZF74 and ZF104 respectively. All undoped and Fe doped powder samples thus obtained after calcination were characterized by different experimental techniques.

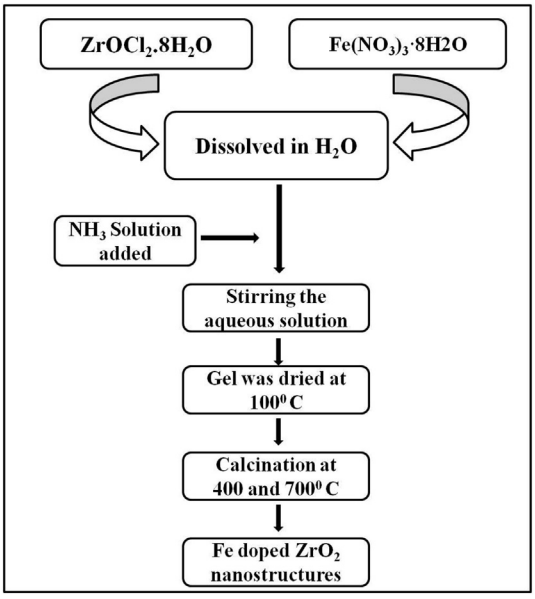

Fig. 1. Synthesis steps used for the synthesis of Fe doped ZrO_2 nanostructures.

2.2. Characterization techniques

The crystalline properties of synthesized powder samples were analysed by XRD measurements using powder diffractometer (Bruker AXS D8) with Cu-Kα radiation (λ = 1.5406 Å) and diffracted signal was recorded for 2θ range 20–80°. The size and shape of the synthesized samples were determined by TEM measurements (Hitachi – H-8100). For TEM measurements, the samples were prepared by dispersing the powder sample in ethanol and the prepared solution is dispersed on carbon coated copper grids. UV–VIS. spectroscopy measurements were carried out to determine the optical band gap of undoped and Fe doped ZrO_2 nanostructures calcined at 400 °C. The samples were finely dispersed in distilled water for UV–VIS. measurements in transmission mode. The absorption spectra of the samples were recorded for the spectral range 200–800 nm with Perkin–Elmer Lambda 35 UV–VIS. spectrophotometer. The PL emission spectra of the synthesized samples were recorded by using a spectro-fluorometer (Spex Flurolog3, FL3-22) with a 450 W Xenon Lamp as the excitation source using 300 nm excitation wavelength. For recording the PL emission spectra, the slit width was kept open for 3.0 nm. The room temperature Raman spectra of the powder samples were recorded in the spectral range, 125–800 cm^{-1} using Thermo Scientific DXR-XI Raman Imaging Microscope. The 532 nm laser line of the Ar^+ ions laser was used to illuminate the powder samples. Vibrating sample magnetometer (VSM) (Microsense EV7) measurements were done to study the magnetic properties of the synthesized samples at room temperature.

3. Results and discussion

3.1. Structural properties

3.1.1. Stabilization of tetragonal phase of ZrO_2 by Fe doping

The XRD patterns of synthesized undoped and Fe doped samples calcined at 400 °C are presented in Fig. 2. All the prominent peaks in XRD pattern are indexed on the basis of JCPDS card no. 80–2155. The undoped and Fe doped samples show same peak profile. The XRD pattern of sample ZP4 reveals six diffraction peaks that are assigned to reflection from (101), (110), (112), (211), (202) and (220) planes. These six peaks are centered at 2θ values 30.2°, 35°, 50.4°, 60°, 62.9° and 74.3°. The indexed XRD peaks confirm the