Materials Science in Semiconductor Processing 17 (2014) 186–193

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Structural, magnetic and charge-related properties of nano-sized cerium manganese oxide, a dilute magnetic oxide semiconductor

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ARTICLE INFO

Available online 25 October 2013

Keywords:
O-DMS
MEM
Charge density
Band gap

ABSTRACT

Nanoparticles of the magnetic semiconductor cerium manganese oxide ($Ce_{1-x}Mn_xO_2$) for six different concentrations of Mn ($x=0$, 0.02, 0.04, 0.06, 0.08 and 0.1) have been synthesized using a chemical co-precipitation method. The obtained samples were characterized for their structural, morphological, optical, magnetic and charge related properties using powder X-ray diffraction analysis (XRD), scanning electron microscopy (SEM) micrograph analysis, UV–visible spectra, vibrating sample magnetometer (VSM) measurements and charge density analysis. Rietveld technique and maximum entropy method (MEM) were used for the analysis of the electron density distribution in the unit cell for the prepared samples. The magnetic behavior of the samples has been explained through charge ordering which are verified using experimental data obtained using vibrating sample magnetometer. The optical absorption analysis done using UV–vis spectrophotometer reveals the existence of both direct and indirect band gaps. Charge density arrangement in the unit cell is correlated to the analyzed properties.

1. Introduction

In recent decades, most of the researchers have concentrated on oxide based semiconductors due to their widely used applications. Ceria based materials are used in many applications such as ceramics, glass polishing, solid oxide fuel cell, photosensitive glass, catalysts, etc. [1,2]. A detailed study shows [3,4] that CeO_2 material is also used in the oxygen storage capacity and this property is enhanced by the introduction of dopant cations like, Ba, Ca, Co, Cu, Mn, Nd, Pb, Sr, Y, Zn and Zr. The high ionic conductivity of doped ceria makes it an attractive electrolyte for solid oxide fuel cells, whose prospects as an environmentally friendly power sources are very promising.

Cerium oxide has received considerable interest because of their high transparency in the visible region, near IR region and electro-optical performance [5]. The ability of cerium-doped glass to block out UV light is utilized in the manufacturing of medical glassware and aerospace windows. In steel manufacturing, it is used to remove free oxygen and sulfur by forming stable oxysulfides [6].

Oxide based dilute magnetic semiconducting (O-DMS) material have attracted much attention because of both magnetic and semiconductor properties causing these materials have great potential for application in magneto-electronic devices [7–9]. ZnO material is most suitable for the spintronics application. CeO_2 arise a possible candidate to the O-DMS because ceria material band gap is nearest to the ZnO. On the other hand, these materials can be used only if they also

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http://dx.doi.org/10.1016/j.mssp.2013.10.002

exhibit ferromagnetic behavior at room temperature. Therefore, the origin of ferromagnetism in these materials is the most sought after one. Some groups [10,11] defend the idea of the existence of magnetic clusters on these O-DMS semiconductors due to segregation of the ferromagnetic phase. All these investigations show that the growth process of the O-DMS can play an important role in the origin and control of the ferromagnetic behavior.

Many methods have been employed to produce doped-cerium oxide nanoparticles such as citrate method [12], ball-milling process [13], chemical precipitation [14,15] hydrothermal synthesis [16] etc. Compared to these methods, precipitation is more attractive due to cheap salt precursors, simple operation and ease of mass production and this method has been used for the authors to prepare Mn doped CeO_2 nanoparticles.

The as-prepared Mn doped CeO_2 nanoparticles have been characterized by XRD techniques for their structural, optical, magnetic and the charge density understanding. The morphology of the prepared nanosystems has been investigated using SEM micrograph at 10,000× magnification. The optical band gap and its dependence on dopant concentration have been studied using UV–visible spectra. The magnetic behavior has also been investigated using VSM measurements and correlated with the other findings.

2. Sample preparation

Mn doped cerium oxide is prepared through chemical route for various concentrations. Initially 5 g of $CeCl_3$ is mixed with 400 ml of double distilled water in a beaker. The solution was stirred using magnetic stirrer at a rapid rate of 500 rpm and kept in a water bath held at 60 °C during the initial synthesis stage. Then 4 ml of ammonium hydroxide is added to the above solution. The pH value of the resulting solution is maintained approximately at 10.5. After 2 h, the heat supply was turned off and the solution was left to spin for another 22 h at room temperature. When the stirring stage was finished, the solution was centrifuged to get the precipitate. The precipitate was again rinsed with double distilled water and sonicated. The above procedure was repeated by taking suitable amount of cerium chloride, manganese oxide and ammonium hydroxide approximately in order to get the resultant stoichiometric product as $Ce_{1-x}Mn_xO_2$; $x=0$, 0.02, 0.04, 0.06, 0.08, and 0.10.

3. Results and discussion

3.1. X-ray profile analysis

O-DMS Semiconducting $Ce_{1-x}Mn_xO_2$ are synthesized using chemical route and X-ray diffractogram was obtained using X-ray diffractometer (PHILIPS) with CuK_α monochromatic beam at Sophisticated Analytical Instrument Facility (SAIF), Cochin University, Cochin in the range of 5–120° with step size of 0.02°. Collected reflections from X-ray diffractometer was subjected to profile fitting using Rietveld technique [17]. The prepared samples show no additional peaks and all the peaks are identified and matched with Joint committee powder diffraction standards (JCPDS) [18]. Observed raw X-ray profile has been refined for the structural changes due to the inclusion of Mn using JANA 2006 software [19]. The software is written on the basis of Rietveld refinement technique which is standard tool for use in the characterization of crystalline materials. The refinement was done considering *fcc* cubic structure for CeO_2 nanoparticles having space group of Fm-3m with 4 atoms per unit cell. Rietveld method uses the refinement of many parameters such as structural parameters, lattice parameters, peak shift, preferred orientation, background profile functions which are used to minimize the difference between calculated profiles and observed profiles. Refined profiles of all the prepared systems are shown in Fig. 1. It shows the perfect profile fitting and the resultant refined structural and other parameters are tabulated in Tables 1 and 2. Table 1 shows a decreasing trend in cell dimensions with increasing dopant concentration of manganese. The variation in cell parameters in doped systems is correlated to the reduction in ionic radius of the dopant material compared to that of host ion [$r_i(Mn^{2+})=0.67$ Å, $r_i(Ce^{4+})=0.92$ Å]. The large difference in the ionic radius is mainly the reason for the decrease in the cell parameters and also for the decrease in volume. However, as the concentration of Mn^{2+} increases, there is an increase in the oxygen ion vacancy which results the decreasing crystal density. Table 2 shows the structure factors extracted from Rietveld refined profile. After extracting the structure factors the values are further used as input in the software PRIMA [22] for constructing charge density distribution in the unit cell using Maximum Entropy Method [23].

Crystallite size of $Ce_{1-x}Mn_xO_2$ is estimated from XRD powder data using GRAIN size software [20] which employs Scherrer formula [21]

$$D_v = \frac{K\lambda}{\beta \cos \theta},$$

where β is FWHM (Full Width at Half Maximum) in radians, k is a constant – usually 0.9, λ is the wavelength used, D_v is the crystallite size (size of the coherently diffracting domain) and θ is the Bragg angle of the reflection. The average crystallite size for $Ce_{1-x}Mn_xO_2$ nanosystems is found to be ~17 nm and the values obtained are tabulated in Table 1. SEM morphological studies are also done for the prepared $Ce_{1-x}Mn_xO_2$ materials and the average particle size is found to be ~280 nm (Fig. 2). From the comparison between grain size estimated from XRD and particle size from SEM, we observe that there may be an average of 18 coherently diffracting domains combines to form single particle.

3.2. Magnetic studies

The prepared doped and undoped CeO_2 nanosystems were characterized for their magnetic properties using vibrating sample magnetometer (Table 3). Hysteresis curve (M vs. H) was drawn for all the nanosystems as shown in Fig. 3 and the magnetic parameters like retentivity, coercivity and saturated magnetization were deduced from the