International Journal of Innovative Technology and Exploring Engineering (IJITEE)
ISSN: 2278-3075 (Online), Volume-9 Issue-4, February 2020

Size and Magnetic Effect of Manganese (Mn) Doped Zirconia (Zro_2) Nanoparticles

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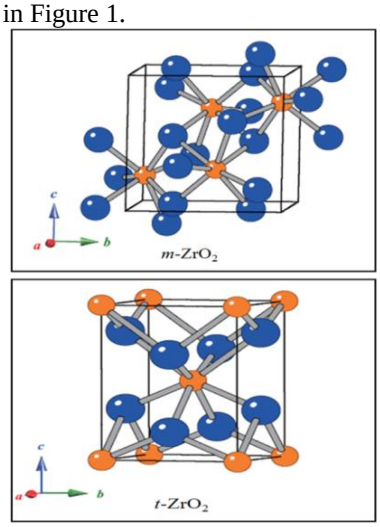
Abstract: ***Un-doped and different mol percentage of manganese doped zirconia nanoparticles were successfully synthesized via precipitation method. The size and magnetic properties of zirconia nanoparticles were systematically analyzed for different mol % manganese in ZrO_2. Obtained results revealed that the manganese (Mn) concentrations played virtual role on various properties of the synthesized ZrO_2 nanoparticles.***

Keywords: ZrO_2, Precipitation method, Dopant effects, Magnetic Properties.

I. INTRODUCTION

Due to excellent properties and applications the metal oxide nanoparticles have been received great attention and worldwide many researcher and their groups were reported importance of metal oxides [1-6]. Large band gap (5 eV) n-type ZrO_2 semiconductor was greatly utilized in the field of electronics and optoelectrics [7-12]. Zirconia exhibits three phase with space group monoclinic: $P2_1/c$, tetragonal: $P4_2/nmc$ and cubic: $Fm\bar{3}m$ respectively. Within these, former two structures are stable at room temperature which is shown in Figure 1.



O=Zr=O

Fig. 1 Crystal structure of Zirconium oxide

Revised Manuscript Received on February 28, 2020.
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In the monoclinic structure, zirconium is surrounded by seven oxygen atoms with the lattice parameter of a:0.5146, b:0.5212, c:0.5313 nm, while in tetragonal structure zirconium atoms are surrounded by eight oxygen atoms, with the same unit-cell structure as the cubic fluorite.[13]. Recently, excellent technological importance as a magnetic, optical and ceramic component the nanocrystalline zirconia has attracted greatly [14]. Out of three different structure of zirconia monoclinic structure alone stable at room temperature with un-doped, the tetragonal phase can be stabilized at ambient temperature with impurity of divalent/trivalent cationic species [15]. Many researchers have been reported as with doping of cations not only stabilized tetragonal structure also the size of the particles decreased with different concentrations. Not only the excellent properties and applications due to the low cost and mass production of the materials, the semiconductor zirconia received much attention. To determine the ferromagnetism of the nanosized semiconductor metal oxide, the size and surface area and surface defects are the most important parameters [16, 17]. Surface defects is most responsible for the observed magnetism, transition metal ion doped metal oxide exhibits large number of surface defects such as oxygen vacancies, because the doping ion playing important role to produce oxygen vacancies [18]. Among various synthesized procedure followed, precipitation process at most control the size and structure of the synthesized materials, hence we adopted with this method. In this present paper we have reported un-doped and three different mole percent age of Mn doped zirconia nanoparticles. The effects of different mole percent age of Mn doped samples were comparatively discussed.

II. EXPERIMENTAL PROCEDURE

In a typical process, zirconium nitrate ($ZrO(NO_3)_2{\cdot}xH_2O$) and sufficient amount of NaOH were dissolved in 100 ml of double distilled water under stirring. The obtained precipitates were collected, washed and dried at 120ºC for more than 12 hrs. Finally, it was calcined at 450ºC for 1 hr to obtain the ZrO_2 samples. The similar way, Mn-doped ZrO_2 samples were prepared by adding of manganese chloride ($MnCl_2$), with different (1-3) mole percentage of Mn in relation to the zirconium content. Chemical equation can easily demonstrate how the final products were formed.

$$ZrO(NO_3)_2{\cdot}xH_2O + 2NaOH \rightarrow 2NaNO_3 + ZrO(OH)_2 + xH_2O \quad (1)$$

$$ZrO(OH)_2 \rightarrow ZrO_2 + H_2O \quad (2)$$

The X-ray diffractometer (JSO-DEBYFLEX 2002) and BHV-55 magnetometer (Riken, Japan) were used to analyse properties of the samples.

III. RESULT AND DISCUSSION

XRD pattern of un-doped and 1, 2 and 3 mol % of manganese doped zirconia are given in Figure 2. The pattern exhibit tetragonal structure of ZrO_2 with peaks at 2θ angle of 30.48°, 35.36°, 50.97°, 60.49° and 63.26° correspond to the (101), (110), (112), (211) and (202) planes [19]. Further, no extra characteristic peaks due to impurities were observed, indicating the high purity of the final product. Interestingly, with increasing Mn concentrations as a dopant the peak intensity and broadness were decreased and increased, respectively. It indicates manganese ions are prevented the growth of zirconia grains in the ZrO_2 latticle.

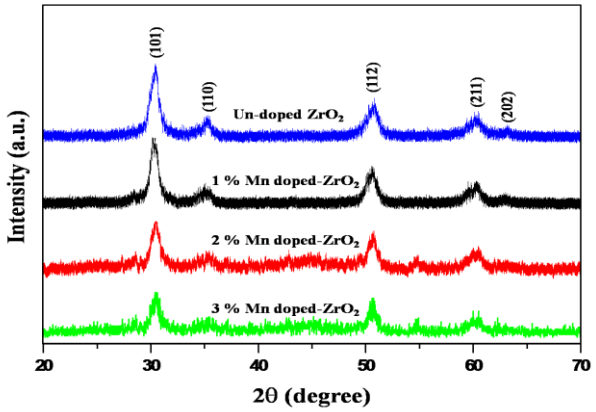

Fig.2 XRD patterns of the un-doped and different mol % of manganese doped zirconia nanoparticles.

Particles sizes were calculated by using Sherrer equation.

$$D = K\lambda/\beta\cos\theta \quad (3)$$

where, θ, β, D and λ are angle, full (F) width(W) at half (H) maximum (M)-(FWHM), particles size and wavelength of X-ray, respectively [20]. The diffraction pattern confirmed that the synthesized samples are in single phase of tetragonal phase of zirconia. The mean crystallite size of un-doped and 1, 2 and 3 mol % of manganese-doped ZrO_2 nanoparticles were measured from XRD peak profile analysis to be 10.6, 9.5, 8.2 and 6.4 nm, respectively. The decreasing particles sizes of the samples are related to the concentrations of the dopant ions. Due to smaller ionic size of Mn (0.66 Å) than that of zirconium (0.72 Å), it can be easily replace the parent atom, hence the size of the final product was decreased. Moreover, it disturbs the crystallographic ordering, hence, dropping crystallite size and produces oxygen (O) vacancies in the zirconia lattice. From the XRD analysis, the crystallite size of 1, 2 and 3 mol percentage of manganese ion doped ZrO_2 nanoparticles were observed to be smaller than that of un-doped ZrO_2 nanoparticles due to Mn concentration at the Zr sites. Hence, 1, 2 and 3 mol % manganese doped zirconia samples alone have been taken to study the magnetic properties.

The effects of manganese concentrations on the magnetic properties of zirconia were examined at room temperature using a VSM technique. The doped metal ions caused three important effects in the host materials, which are local magnetic moment, differences in valance state and impurity conduction in the host [21]. As shown in Fig. 3 (a-c), the linear relationship between the magnetization and applied magnetic field can be observed. The 1 and 2 mol % of Mn concentrations into the ZrO_2 particles favour the superparamagnetic behaviour (Fig. 3 (a-b)); however, at higher concentration (3 mol %) the particles possess the ferromagnetic behavior, as shown in Fig.3 (c), which may be due to the higher oxygen vacancies [22, 23]. Moreover, the transition metal ion doped ZrO_2, lead to higher coercivity. In the present case, the coercivity values were observed 55.253, 84.628 and 128.34 G for 1, 2 and 3 mol % of manganese doped ZrO_2, respectively. Comparison of XRD and magnetic studies were presented in Table-I. Therefore, transition metal ion Mn^{2+} influences the magnetic properties of ZrO_2 nanoparticle, and hence, it is a capable material for spintronic devices [24, 25].

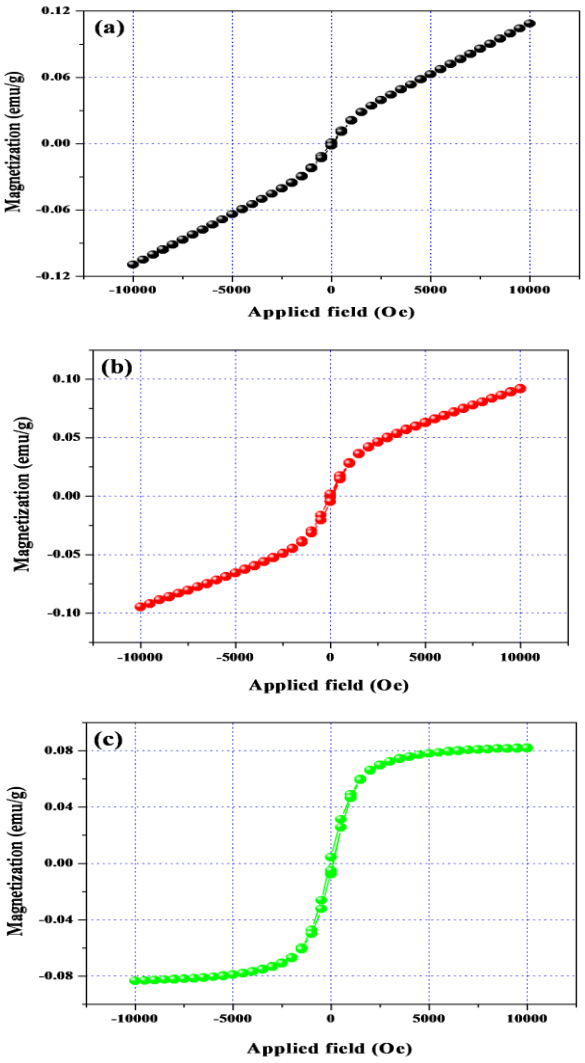

Fig.3 Magnetic properties of different mol % of manganese doped zirconia.

Table- I: Comparisons of un-doped and Mn-doped ZrO2 nanoparticles

Name of the sample	Particle size (XRD)nm	Magnetic studies	
		Behavior	*Coercivity (G)*
Un-doped ZrO_2	10.6	-	-
1 % Mn-doped ZrO_2	9.5	superpara	55.253
2 % Mn-doped ZrO_2	8.2	superpara	84.628
3 % Mn-doped ZrO_2	6.4	ferro	128.34

Moreover, dopant and dopant concentrations, defect levels in the materials are the responsible for the ferromagnetism of the synthesized samples. The 3 mol % of Mn doped sample shows ferromagnetic behaviour clearly than that of other two samples, which might be the greater density of oxygen (O) vacancies, are presented in sample. When the manganese concentrations are increased from 1 mol % to 3 mol % which substituted in large manner for zirconium ions sites, during the substitution compensation of anionic vacancies are formed in the O^{2-} sub-lattice. These vacancies are main reason for ferromagnetism obtained in higher concentration of manganese doped zirconia nanoparticles.

IV. CONCLUSION

In summary, un-doped and 1, 2 and 3 mol % of manganese doped zirconia (ZrO_2) nanoparticles were successfully prepared via facile precipitation method. From the XRD results, it was found that the crystallite sizes of the synthesized samples were decreased with the increase in dopant (Mn) concentrations. The dopant concentrations induced ferromagnetic properties in the material; among the samples the greater density of oxygen vacancy of 3 mol % Mn doped zirconia higher ferromagnetic behaviour than that of the other two samples. Hence, the narrow size distribution nanoparticles and enhanced ferro-magnetic properties of manganese doped zirconia nanoparticles synthesized via precipitation method make it particularly appealing for technological applications and optoelectronic devices.

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