Preparation of Nanometer sized Mn doped Zn based oxides powder for DMS applications

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ABSTRACT

In order to study the size dependent DMS (Diluted Magnetic Semiconductor) behavior of Mn doped ZnO , we have systematically prepared a series of nanosized green powder based on Mn doped ZnO ($Zn_{1-X}Mn_XO$,where x= 0.02 – 0.1) materials using our novel and low cost pyrophoric reaction technique route [16] . Microstructural (TEM) analysis of the green powder were carried out to understand the surface morphology, particle size and crystalline behavior (if any) of the green powders. It is observed that average particle size down to 20nm were formed by the Pyrophoric Reaction Technique Route which are the potential entity for the formation of high density nanostructured sintered ceramic target for preparation of ultra thin films of Zn based Diluted Magnetic Semiconductors (DMS).

INTRODUCTION

Diluted Magnetic Semiconductors are a novel class of semiconducting materials in which cations are partially replaced by magnetic atoms. The materials are commonly known as semimagnetic semiconductors (SMSC) or diluted magnetic semiconductors (DMS). Strong exchange interactions between extended *sp* carriers of the host semiconductor bands and a localized *d* electron of the magnetic ions (mostly transition metal) cause interesting spin dependant optical and electrical properties [1]. In fact, DMS, combining charge with spin degrees of freedom, have recently [2,3] been of intense focus as the ideal materials for spintronics devices, such as spin valve transistors, spin light emitting diodes, spin polarized lasers, non-volatile memories, magneto-optical switches etc.. As known, ZnO is one of the versatile and important oxide materials due to its typical properties such as resistivity control over the range 10^{-3} to 10^{-5}ohm-cm,transparency in the visible range, high electrochemical stability, direct wide band gap (3.37eV) semiconductor with a high excitation binding energy of 60 meV, absence of toxicity and its abundance in nature. Recently, ZnO based DMSs have attracted much more attention due to the theoretical prediction of

room temperature (RT) ferromagnetism (FM) in p-type Mn doped ZnO($Zn_{1-x}Mn_xO$) [4]. Also as mentioned ZnO is transparent in the visible region, making transparent ferromagnet is also possible. There have been several experimental works on $Zn_{1-x}Mn_xO$ thin films [5-9], powders [9-11],nanostructures[12-14],&bulks[15].However, the contradictory conclusions including paramagnetic, ferromagnetic and antiferromagnetic behavior were obtained [6,7,9-15]. The inconsistent results indicate that the magnetic properties of $Zn_{1-x}Mn_xO$ are highly sensitive to the preparation technique and conditions. In fact, depending upon the different growth modes and mechanisms, microstructures in ZnMnO system, such as the distribution of Mn ions in ZnO crystal lattice and the local environment around Mn ions are very different, which considerably affect the magnetic properties of $Zn_{1-x}Mn_xO$.

In an attempt to engineer the material towards achieving theoretically predicted room temperature ferromagnetism, we have synthesized a series of Mn doped ZnO materials by solid state reaction technique as well as pyropheric reaction technique. Apart from varying the doping concentration of manganese in ZnO, attempt has also been made by our group for co-doping rare earth elements in ZnO: Mn system. In this communication, we report preparation of nanometer sized Mn doped ZnO powders as well as the results of the co-doping of samarium (Sm) into the ZnO: Mn system.

EXPERIMENTAL

High pure (99.999%) oxides of Zinc, Manganese and rare earth elements were taken in powder form to prepare Mn doped ZnO and Sm co-doped ZnO: Mn system. Appropriate proportion of the metal oxide powders with following composition were taken, mixed and ground. The powders were initially heated at 450^0C followed by RT quenching and grinding. After four times of grinding and quenching cycle at 450^0 C, powders were palletized using hydraulic press at the pressure of 8 ton/ cm^2 . In addition to this, green powders of above mentioned appropriate proportions were prepared by pyropheric reaction technique developed by us[16].The powders thus palletized (2-3mm thickness & 10mm diameter) were sintered at high temperature (approx. 1300^0 C) for obtaining high density sintered product, which are characterized by XRD,TEM &SQUID magnetization measurements. Important and interesting results pertaining to our above mentioned material system (ZnO: Mn, ZnO : (Sm, Mn)) are presented and discussed in the text.

RESULTS AND DiSCUSSIONS

Fig.1 (a, b, c) shows the TEM photographs of as prepared green powders by pyropheric reactions for different compositions. It is clearly observed from the TEM analysis that isolated particles with approximate dimensions upto 20nm are produced by the pyropheric technique. It is also observed that insignificant particle growth beyond 25-30 nm does not occur, as Mn doping concentration in ZnO system ranges from 0.02 to 0.1. However, in the case of Mn concentration

of 0.05 in ZnO, the average particle size limited to the least dimension of 20 nm. No significant agglomerations of the particles were found. After sintering at high temperature (aprox.1300^{0}C), highly crystalline grain growths have been observed with larger particle size.

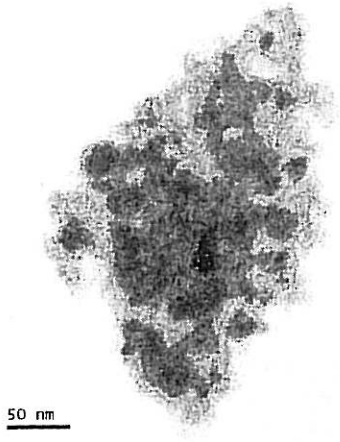

Fig.1a $Zn_{1-x}Mn_xO$. (x=0.01)

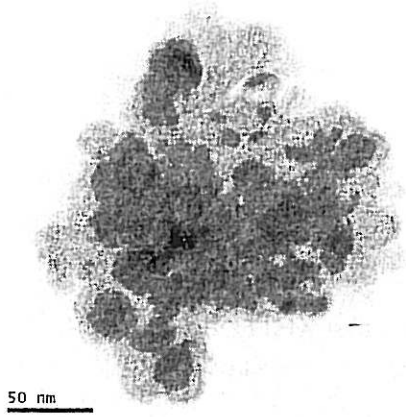

Fig. 1b $Zn_{1-x}Mn_xO$.(x=0.04)

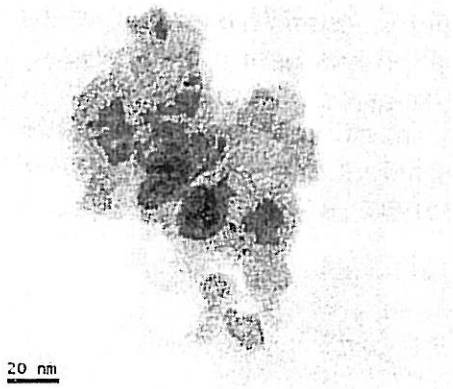

Fig 1.c $Zn_{1-x}Mn_xO$.(0.05)

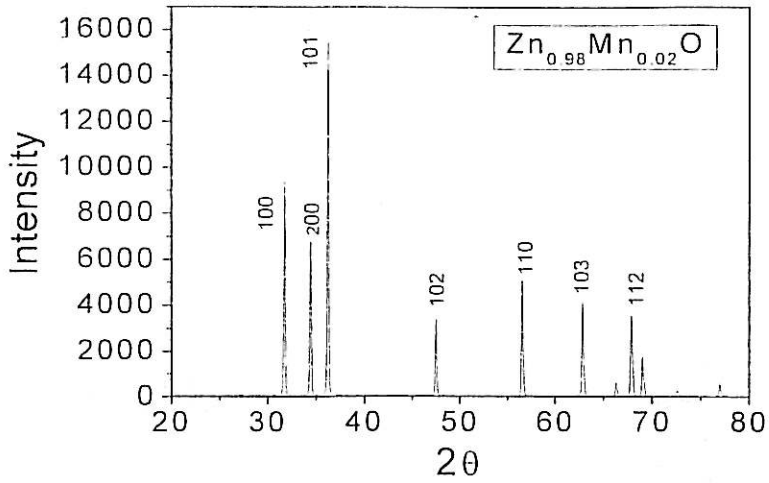

Fig. 2

Fig.2 shows the XRD pattern of the sintered $Zn_{1-x}Mn_xO$ material (x=0.02). The X-Ray lines are indexed. Sharp XRD peaks at lower 2θ angle clearly exhibit the prominent crystalline character of the sintered specimen.

M~H plot at room temp. (300K) & 10K of Sm co-doped ZnMnO samples are shown in Fig.3a & 3b respectively. It is noted from Fig 3a that there exist a linear relationship between M & H specially within the magnetic field of ± 2KOe range. No saturation magnetization signal has been found. However, at low temp., down to 10K, there is a distinct magnetic hysteresis at low field region and a tendency of magnetisation saturation has been noted beyond the magnetic field of 5 KOe. This behavior clearly indicates ferromagnetic character associated with the Sm co-doped ZnMnO system. Attempt has been made to enhance the temp. scale upto 300K by adopting different processing parameters as well as optimizing the rare earth (RE) co-dopants.

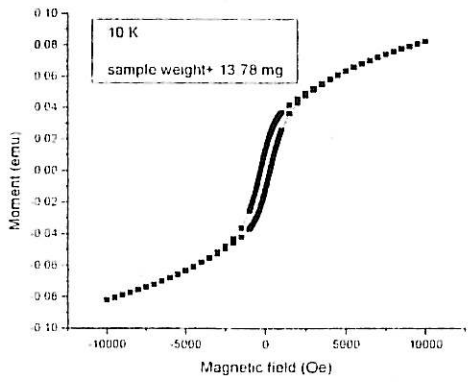

Fig-3a

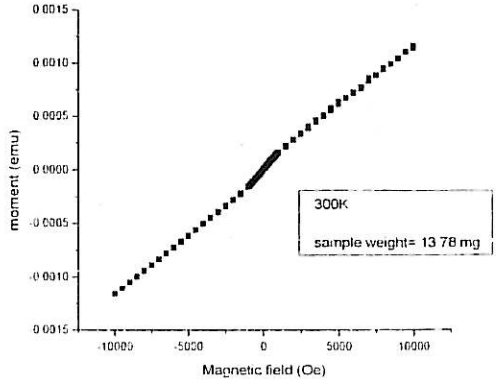

Fig-3b

CONCLUSION

We have demonstrated the feasibility of producing nanometer sized Mn doped Zn based oxide powders down to 20nm scale by using novel pyropheric reaction technique. It is highly encouraging to note the possibility of engineering rare earth (RE) (Sm,Gd,Eu,Ce,...) co-doped ZnMnO system to achieve ferromagnetic behavior at low temperature which can be enhanced upto room temperature by adopting different processing parameters as well as optimizing the RE co-dopants.

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