Preparation and Characterization of Mn and Co substituted nanoparticle ZnO

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ABSTRACT

With a view to investigate the influence of nano size on various physical properties of transition metal substituted ZnO, a series of materials were prepared by different chemical routes viz; Citrate gel, polyvinyl alcohol (PVA ) precursor and Chemical solution decomposition (CSD) methods.

In the citrate gel method, the starting materials were nitrates and ethylene glycol acts as a gelating reagent. In the PVA method also the starting materials were nitrates and equal weight of PVA is added to the mixture. This was dissolved in distilled water and stirred thoroughly and burnt to get nano powders of the product. In the third method (CSD), the ingredients were taken stoichiometrically and mixed together. The precursor solution was obtained by adding triethanolamine (TEA) and after evaporation; the resin was burnt to get nanopowders.

Finally, all the materials prepared under different routes were characterized structurally by X-ray diffraction (XRD) technique. The XRD data were analyzed by Rietveld refinement technique and are found to crystallize into wurtzite crystal structure.

The average crystallite size values estimated using Scherrer formula and are found to be in the range of 15-40 nm. It has been concluded that PVA precursor method is more appropriate to prepare nano size particles of Oxide diluted magnetic semiconductor (ODMS) materials.

Keywords: citrate gel, nano crystallite, x-ray diffraction, spintronics

1 INTRODUCTION

Diluted magnetic semiconductors (DMS) are non-magnetic semiconductors doped with magnetic impurities such as Fe, Co, Ni etc; resulting in exhibiting two interesting properties viz; semi conducting as well as magnetic. In recent years, Diluted magnetic semiconductors (DMS) have attracted a lot of enthusiasm and interest due to possibility of manipulating charge and spin degrees of freedom in a single material. Recently, transition metal-ion-doped oxide semiconductors, such as ZnO, TiO$_2$, SnO$_2$, and HfO$_2$ have been investigated extensively [1–4]. Unlike the diluted magnetic semiconductors based on III–V or II–VI semiconductors showing ferromagnetism only at very low temperatures, these oxide-based DMSs exhibit ferromagnetism at higher temperatures well above the room temperature. They are also optically transparent enabling them to be promising candidates for magneto-opto-electronic applications. However, an intrinsic origin of the ferromagnetism in these oxide-based DMSs is still under debate. The mechanisms such as carrier induced double-exchange and new exchange mechanism involving donor electrons in an impurity potentially play a role depending on the conductivity type and level in the material [5,6]. Among other oxide-based DMS, ZnO doped with small amount of Mn and Co without any modification in the structure have been the materials with considerable interest.

It is well known that nano size has great influence to the performance of several material systems. In recent years, nano structures based on ZnO, TiO$_2$, SnO$_2$ etc; have attracted much attention. Further, one can also visualize that nano size might influence various physical properties of not only the host semiconductors but also the DMS materials derived out of them. In fact, recently it was reported [7] that when the size of Co doped ZnO diluted magnetic semiconductor is reduced to about 60nm, the material is found to exhibit better ferromagnetic properties when compared with those ones having micro crystalline particles. Similarly, it was also observed [8] the presence of even super para magnetism among Co doped ZnO DMS materials. Moreover, nano crystalline DMS material can also be exploited as ferro fluids, biomedical & magnetic recording devices etc: Further, DMS materials with nano crystalline structure are also expected to boost the storage industry where smaller particles are essential. Therefore, the subject of investigating the ferromagnetic behavior of nano crystalline DMS materials is very interesting and important. Thus basic understanding of the influence of nano size on ferromagnetic behavior of DMS materials will be useful in exploiting the materials with improved properties for variety of applications. Therefore, a systematic study of nanocrystalline oxide DMS materials has been undertaken and the results of such an investigation are presented here.

2 EXPERIMENTAL METHODS FOR THE PREPARATION OF SAMPLES

2.1 Citrate gel method

Although many preparation techniques exist for the preparation of ZnO based DMS material, an effort has been made to prepare the materials using three different techniques viz., Citrate-gel, polyvinyl alcohol (PVA) and Chemical solution decomposition (CSD). Therefore, polycrystalline samples of Zn$_{0.9}$TM$_{0.1}$O (TM= transition metal ions such as Mn , Co etc; )
were prepared by Citrate-gel process by taking the corresponding starting materials as nitrates. The stoichiometric nitrates in solution are converted into citrates and the pH is adjusted to 6.5. After getting a sol on slow evaporation, a gelating reagent ethylene glycol is added and heated at 160-180 °C to get a gel. This on further heating yields a dry fluffy porous mass (precursor), which is calcined at 250 °C for 3 hrs. The powder is pressed into circular pellets of 10mm diameter and 1.2mm thickness. Pellets were sintered in air atmosphere at different temperatures (300°C, 400°C, 500°C and 600°C) for 3 hrs at the rate of 5°C/min. and then the furnace is cooled to room temperature. This method gives good homogeneity, controls the grain size.

2.2 PVA method

Polyvinyl alcohol (PVA) is taken in 1:1 weight ratio of the final product and is dissolved in distilled water and stirred thoroughly around 50°C for 3-4 hrs. Now, the starting materials were taken as nitrate solutions and are slowly added to the PVA solution. The final solution is slowly evaporated on hot plate till it becomes solid mass which is burnt to get nanopowders.

2.3 Chemical solution decomposition (CSD) method

In this method ZnO was dissolved in dilute nitric acid and was mixed with water solution of Co(No)₂₆H₂O or Manganous acetate were taken in corresponding molar ratio. To the mixed solution of the metal nitrates, a complexing agent triethanolamine (TEA) was added taking 3 mol of TEA per mol of metal ion. The solution is stirred thoroughly and heated on a hot plate till it formed a solid mass. It was burnt to get nanopowders.

3 RESULTS AND DISCUSSION

The Crystal structure of Zn₀.₉₅TMₐ₀.₀₅O (TM= Mn & Co) were determined using X-ray diffraction (XRD) with Philips (Xpert) diffractometer using CuK radiation. Figs.1 (a) and 1(b) show typical XRD patterns of Mn and Co doped ZnO sample prepared by using three different techniques. The XRD data were analyzed by Rietveld refinement technique and is a typical plot is shown in Fig. 1(c).

All the samples studied are found to exhibit wurtzite structure. No additional peaks were observed which would correspond to any impurity phase.

The average crystallite size (S) values were calculated using the XRD data and while doing so, instrumental errors and processing conditions were taken into consideration. The broadening of reflections due to micro-strains was considered to have an angular dependence of the form,

\[ \beta_{\text{Strain}} = \varepsilon \tan \theta \]  

where \( \beta_{\text{Strain}} \) is the peak shift due to strain (\( \varepsilon = \Delta d/d \)) is the coefficient related to strain and \( \theta \) is Bragg angle. The dependence of size effect can be given by the Scherer formula,

\[ \beta_{\text{Size}} = K \lambda / t \cos \theta \]  

where, \( K \) is the grain shape factor (for a spherical grain \( K = 0.89 \)), \( \lambda \) is wavelength of Cu Kα radiation (\( \lambda = 1.5406\)Å), \( t \) is thickness of the crystal. The instrumental broadening effect has been eliminated, by subtracting the value of full width at half maxima (\( \beta_s \)) corresponding to a standard sample (SiO₂) from \( \beta_{\text{Size}} \) at respective Bragg peaks. The complete expression for the full width at half maximum is a linear combination of strain and size broadenings and is given by.
\[
\beta_{\text{Nuc, Strain}} = \varepsilon \tan \theta + K \lambda / t \cos \theta
\]  
(3)

From this equation, the average crystal sizes have been calculated and are given in Table 1.

Table 1. Crystallite size values of samples prepared by various methods.

<table>
<thead>
<tr>
<th>Method of Preparation</th>
<th>( \text{Zn}<em>{0.9}\text{Co}</em>{0.1}\text{O} ) (&lt;S&gt;) nm</th>
<th>( \text{Zn}<em>{0.9}\text{Mn}</em>{0.1}\text{O} ) (&lt;S&gt;) nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citrate-gel</td>
<td>30</td>
<td>28</td>
</tr>
<tr>
<td>PVA</td>
<td>20</td>
<td>16</td>
</tr>
<tr>
<td>CSD</td>
<td>45</td>
<td>40</td>
</tr>
</tbody>
</table>

Surface morphology studies of the samples were done using Pico-LE Microscope of 1nm resolution. Typical images of the samples are shown in Figs. 2.

![AFM image of Zn\(_{0.9}\)Co\(_{0.1}\)O (30nm) and Zn\(_{0.9}\)Mn\(_{0.1}\)O (20nm) samples.](image)

Magnetizations versus magnetic field measurements of all the samples were carried out using a Vibrating Sample Magnetometer model No. DMSADE - 1660 MRS at room temperature and are found to exhibit hysteresis at room temperature. Figs. 3 shows M-H loop of Co doped ZnO prepared using PVA and citrate gel methods. The saturation magnetization values for the sample Zn\(_{0.9}\)Co\(_{0.1}\)O prepared by citrate gel and PVA routes are about 0.05 emu/g, while that prepared by TEA route is 0.02emu/g. However, the coercivity values are found to be negligibly small. The observed ferromagnetism in the samples of the present investigation is considered to originate from the exchange interaction between free delocalized carriers (holes or electrons from the valence band) and the localized d spins on the TM ions [9]. Therefore, the presence of free carriers and localized d spins is a prerequisite for the appearance of ferromagnetism.

![Magnetization versus magnetic field measurements.](image)

Figure 3. Room Temperature M-H curve of Zn\(_{0.9}\)Co\(_{0.1}\)O sample prepared by PVA and Citrate method. Inset figure shows the magnified image of the same.

CONCLUSIONS

The authors of the present investigation were able to synthesize some nano crystalline oxide based diluted magnetic semiconductors using three different chemical methods. Compared to other two methods, PVA method is found to produce materials with smaller nano crystallite sizes. The M-H loop trace gives a clear cut message that the materials under investigation are having room temperature ferromagnetism.

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