

SYNTHESIS AND ELECTRICAL TRANSPORT PROPERTIES OF METAL OXIDE NANOMATERIALS

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I. INTRODUCTION

Metal oxides play a crucial task in several areas of physics, chemistry and material sciences. The elemental metals can form varieties of oxide compounds[1–4]. This variation can occur due to structural geometry, multi-valancy, doping effect etc. They can implement different geometrical structure with an electronic structure that can show metallic, semiconductor or insulator character. Metal oxides semiconductor draws a scientific attention due to their intrinsic worth in multipurpose fields applications such as catalysis ,energy conversion, magnetic memory devices ,batteries, solid oxide fuel cell optoelectronics devices, piezoelectric , solar cells , biomedical fields, gas sensors , luminescent LCDs and semiconductor devises etc[5–7]. Nanostructured materials are more competent due to their enhanced properties, compared to its bulk counterpart. In few decades, researchers around the globe widely studied the effect of transition metal (, Cr, Ni, Fe, Co, Mn etc.) doping on semiconductor oxides. In this way the host material becomes the dilute magnetic semiconductor (DMS) due to the substitution of cations by the transition metal ions.

II. SYNTHESIS OF OXIDE NANOMATERIALS

To study the oxide nanomaterials, the first requirement is to synthesis of the material. For the synthesis of nanostructured materials; generally, there are two broad categories of approaches. First one is bottom-up approach; in which the tiny materials components up to the atomic level self-assembled to form the nanostructured material. In this process quantum dot or nanoparticles are formed by organizing the atomic or molecular components from wet chemical method.

Wet chemical synthesis methods allow us to achieving preferred morphology and phase of oxide nanoparticles leading to desired properties for possible applications[8].The wet chemical synthesis process is a highly controlled process for maintaining the quality of the metal oxide nanoparticles. Samapti et.al have prepared ZnO nanorods [9], Yan et. Al have prepared CeO₂nanoparticles[10], Li et al have prepared Co₃O₄[11]by wet chemical method. Their precursor components were sodium hydroxide pellets, ammonium peroxodisulphate and Zinc metal powder.

The second broad type approach is Top-down approach; this approach initiate with bulk material and nanostructure is formed by controlling the process externally. Mechanochemical process is involved with the chemical reactions and structural deformations induced by the application of mechanical high energy [12]. Mechanical alloying

is an effective and popular modern age Top-down method of nanomaterial synthesis. It is generally accomplished in a high energy ball mill and thus it is also called high energy ball milling. This 'high energy' comes from the high speed of the mechanical mill, impact of the balls and pot, melting, plastic deformation or pressure. The mechanical alloying is a process by which the constituent powders are iteratively fractured, deformed and re-welded to form a homogenous alloyed microstructure of dust particles in a high energy ball mill. Synthesis of oxide nanomaterial in air atmosphere is advantageous in the point of view of oxidation effect from the open environment. There are so many reports of dry synthesis of oxide nanoparticles by mechanical alloying (MA) in open air at room temperature using a high energy planetary ball mill; such as synthesis of Mn doped ZnO nanopowder[13], manganese (Mn) doped CeO₂ nanomaterials [14] by the Mechanochemical process. The X-ray diffraction (XRD) patterns of without milled ZnO and ball milled manganese (Mn) doped ZnO samples are shown in Figure 1.

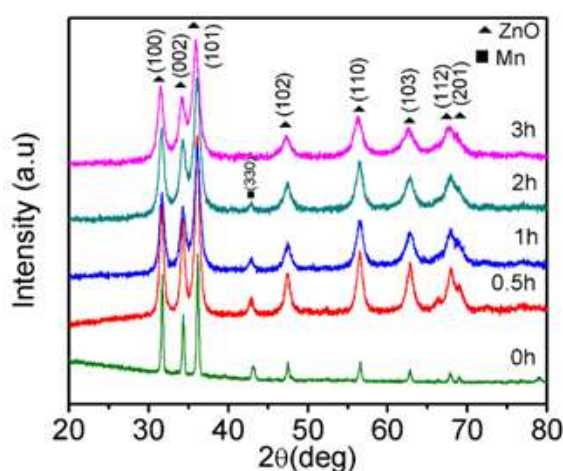


Figure 1: XRD patterns of without milled (0h) and different duration ball milled manganese doped ZnO nanocrystallites.

III. ELECTRICAL TRANSPORT PROPERTIES OF OXIDE NANOMATERIALS

For the application of nanomaterials, it is extremely essential to recognize the different properties of the materials. The study of electrical properties of nanomaterial is compulsory for the electronic based application. The properties of any material are associated with its atomic structure and electromagnetic structure. The outermost electrons of the atoms take part in the electrical conduction phenomena. The electrical properties of nanomaterial is based on the composition, shape, size and charge concentration of the crystallites [15,16]. By controlling the charge carrier density one can control the electrical properties of the nanomaterial. The electrical and dielectric properties of nanostructured materials differ from those of bulk or micron sized materials due to increased number of atoms at the interface and presence of defects at grain boundaries[17]. Since each interface acts as a capacitor, consequently the dielectric value alters significantly with the varying contribution from grain boundaries. The electrical conductivity of a polycrystalline material is the sum of the contribution from all the charge carrier transport under the applied field. The dc electrical conductivity can be measured by applying a dc voltage across the pellet formed by the

sample. However, the ac conductivity and dielectric property can be investigated as a function of temperature and frequency by applying an ac voltage.

Oxide based materials can show ionic and electronic or diverse electronic / ionic conduction influenced by the nanostructure, doping element, stoichiometry and presence of disorder in the material. According to the Maxwell-Boltzmann statistics, the number of charge carriers in a metal oxide material is highly depend on the band gap energy. When a material is placed in an electric field, the charge carriers in the material responses with the field and electrical conductivity arises. In the well-known metals and semiconductor type conductors, electronic conductivity is described due to the movement of charge i.e electrons or holes. The electronic conduction is referred to as n hopping-type when the principal charge carriers are electrons and is referred to as p hopping-type when the principal charge carriers are holes. The tunneling transitions from occupied to unoccupied localized states occurred during hopping. The emission or absorption of one or several phonons is associated with the energy difference of the states. Introduction of non-stoichiometry can enhance the number of free electron or holes in an oxide material and balanced by the creating oxygen/cation vacancies. The temperature dependence of dc conductivity (σ_{dc}) for the three dimensional materials can be expressed by the Godet variable range hopping theory (3D G-VRH) [18,19],,

$$\sigma_{dc}(T) = \sigma_{00} \exp \left(-\frac{T_0}{T} \right)^{1/4} \quad (1)$$

σ_{00} = constant and T_0 = Godet characteristic temperature.

The hopping energy (W) depends on the average hopping distance (R)[20,21]. The average hopping distance (R) is a function of the density of state (DOS) and the distribution of charge. The activation energy of conduction of the material and the average hopping distance (R) is inversely related with the size of crystallites. The fitting of the model in case of Mn doped ZnO nanocrystallite is justified by the linear relationship between $\ln\sigma_{00}$ and $T_0^{1/4}$ or exponential relation between σ_{00} and $T_0^{1/4}$ in Figure 2.

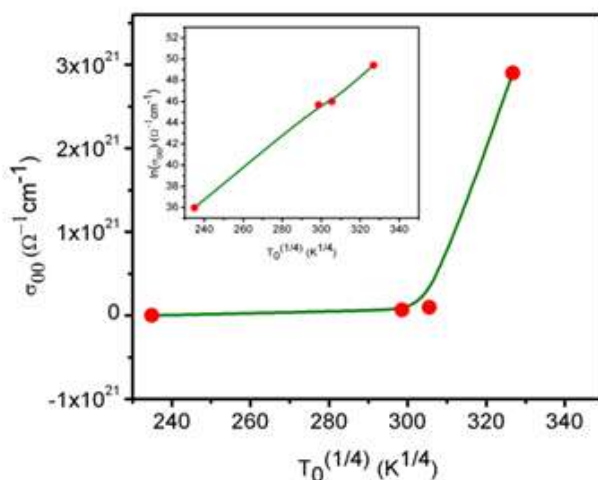


Figure 2: Variations of (σ_{00} vs $T^{-1/4}$) and ($\ln\sigma_{00}$ vs $T^{-1/4}$) for manganese doped ZnO nanocrystals

The charge carrier density and mobility of charge carriers are significantly low in the lower temperature region. So, the temperature dependence dc conductivity is mainly depending on the intrinsic nature of the material. But with the increase of temperature, the material particles are thermally excited, as a result both the charge carriers density as well as mobility increases from the defects level. In semiconductor nanomaterial which have different type of disorder, they exhibit electrical transportation through localized electronic states near a so-called ‘transport level’ in low temperature region. The transport level is mainly depends on the position of the Fermi level shape of the density of state (DOS), and temperature of the sample. In high temperature region, the major defect states in ZnO nanocrystal are zinc interstitial (Zn_i) and oxygen vacancies (V_o) which act as donor in ZnO. These donor levels transfer excited electrons to the conduction band, as a result conductivity increases. In case of Mn-doped CeO_2 nanocrystal, the frequency dependence of the real part of the ac conductivity $\sigma'_{ac}(f)$ at different temperatures [22] are shown Fig.3. The real part of the ac conductivity is calculated using the equation $\sigma'_{ac}(f) = 2\pi f \epsilon' \tan \delta$.

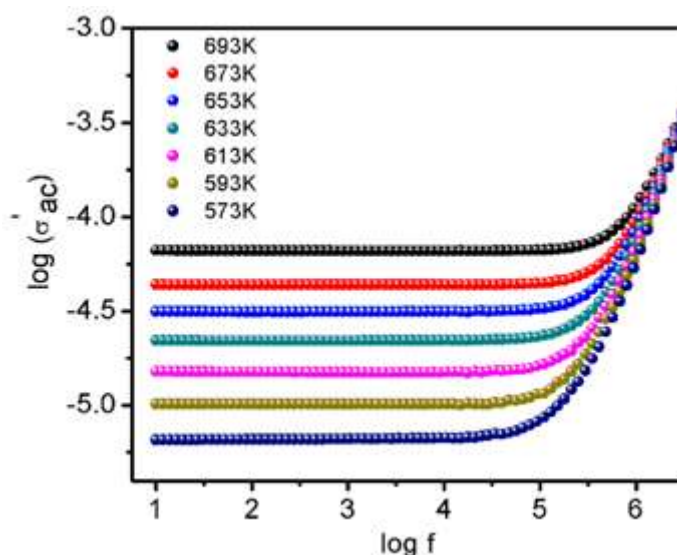


Figure 3: Plot of $\sigma'_{ac}(f)$ of Mn-doped CeO_2 nanocrystals at different temperatures

Another type of electrical conductivity such as ionic conductivity arises due the motion of ionic charge. Similar to hopping-type conduction, due to thermal activation, the ionic conduction takes place when ions can hop from site to site within a crystal lattice, and is usually understand on the basis of a modified Fick’s second law. Generally, the ionic conduction occurs in a liquid electrolyte solutions. In case of solids this type of conductivity being used to interpret the phenomena of corrosion. In recent times, the applications of ionic conduction have been found in energy conversion devices and chemical sensors[23].

Ionic conductivity is mainly depends on three factors such as the carrier charge (q), the concentration (n) and the mobility (b) and related as

$$\sigma = qnb$$

IV. SUMMARY AND PROSPECTS

In the recent few decades, the research and advancement of different methods of giving out to synthesize metal-oxide nanoparticles have made significant improvement. A variety of metal-oxide nanoparticles including doped oxides and composite oxide, have been investigated by controlling particle size and shapes. Although synthesis of metal-oxide nanoparticle has become a research field of its own, processing of metal-oxide nanoparticles has not yet reached its maturity. In the process of translation of lab scale synthesis to industrial scale production faces many challenges. Future research is necessary to overcome the challenges.

REFERENCES

- [1] M. Fernández-García, A. Martínez-Arias, J.C. Hanson, J.A. Rodriguez, *Chem. Rev.* 104 (2004) 4063–4104.
- [2] A.F. Wells, *Structural inorganic chemistry*, *Nature*. 229 (1971) 453.
- [3] W. Stumm, *Transition metal oxides: surface chem. and catalysis*, *Adv. Colloid Interface Sci.* 35 (1991) 198.
- [4] N.M. Harrison, C. Noguera, *Acta Crystallogr. Sect. A Found. Crystallogr.* 53 (1997) 855–856.
- [5] K. Zhang, N. Zhu, M. Zhang, L. Wang, J. Xing, *J. Mater. Chem. C*. 9 (2021) 3795–3799.
- [6] T. Miyasaka, A. Kulkarni, G.M. Kim, S. Öz, A.K. Jena, *Adv. Energy Mater.* 10 (2020) 1–20.
- [7] K. Keis, C. Bauer, G. Boschloo, K. Westermark, H. Rensmo, H. Siegbahn, *Chem.* 148 (2002) 57–64.
- [8] A. V. Nikam, B.L.V. Prasad, A.A. Kulkarni, *CrystEngComm*. 20 (2018) 5091–5107.
- [9] S. Kundu, S. Sain, B. Satpati, S.R. Bhattacharyya, S.K. Pradhan, *RSC Adv.* 5 (2015) 23101–23113.
- [10] B. Yan, H. Zhu, *J. Nanoparticle Res.* 10 (2008) 1279–1285.
- [11] L. Li, J. Ren, *Mater. Res. Bull.* 41 (2006) 2286–2290.
- [12] T. Tsuzuki, *Commun. Chem.* 4 (2021).
- [13] A. Dhara, S. Sain, S. Das, S.K. Pradhan, *Ceram. Int.* 44 (2018) 7110–7121.
- [14] A. Dhara, S. Sain, P. Maji, S. Das, S.K. Pradhan, *Solid State Sci.* 87 (2019) 93–100.
- [15] G.Y. Yurkov, A.S. Fionov, Y.A. Koksharov, V. V. Koleso, S.P. Gubin, *Inorg. Mater.* 43 (2007) 834–844.
- [16] R. Gangopadhyay, A. De, *Chem. Mater.* 12 (2000) 608–622.
- [17] S. Ramasamy, B. Purniah, *PINSA*, 67 (2001) 85–102.
- [18] C. Godet, *Phys. Status Solidi Basic Res.* 231 (2002) 499–511.
- [19] C. Godet, *J. Non. Cryst. Solids*. 299–302 (2002) 333–338.
- [20] K. Omri, I. Najeh, L. El Mir, *Ceram. Int.* 42 (2016) 8940–8948.
- [21] A. Dussan, R.H. Buitrago, *J. Appl. Phys.* 97 (2005) 10–15.
- [22] A. Nandy, C.S. Tiwary, A. Dutta, K. Chattopadhyay, S.K. Pradhan, *Electrochim. Acta.* 170 (2015) 360–368.
- [23] B.C.H. Steele, *Solid State Ionics*. 129 (2000) 95–110.