**Synthesis and Electrical transport properties of Metal Oxide Nanomaterials**

Arup Dhara\*

*Department of Physics, Burdwan Raj College, Burdwan 713104, West Bengal, India.*

Email: arupdhara2010@gmail.com

1. **Introduction:**

Metal oxides play a crucial role in many areas of physic, chemistry and material sciences. The metal elements can form varieties of oxide compounds[1–4]. This variation can occur due to structural geometry, multi-valancy, doping effect etc. They can adopt different structural geometry with an electronic structure that can exhibit metallic, semiconductor or insulator character. Metal oxides semiconductor draws a major interest due to their merits in versatile applied fields such as optoelectronics , piezoelectric , memory devices , solar cells , UV detectors , gas sensors, field effect transistor , catalysis , solid oxide fuel cell, electro-optic devices, luminescent liquid crystal displays , semiconductor devises and biomedical fields etc[5–7]. Nanostructured materials are more efficient due to their improved properties, compared to its bulk counterpart. In recent years, several researchers extensively studied the influence of transition metal (Fe, Mn, Ni, Cr, Co etc.) doping on semiconductor oxides, in which transition metal ions substitute cations of the host material and form the dilute magnetic semiconductor (DMS).

1. **Synthesis of oxide nanomaterials:**

To study the oxide nanomaterials, the first requirement is to synthesis of the material. There are in general two types of approaches for the synthesis of nanostructured materials. A bottom-up approach that includes miniaturization of materials components up to atomic level with further self-assembly process leading to the formation of nanostructures. This approach organizes atomic or molecular components in hierarchical nanocomplexes. Such examples are QDs or nanoparticles formed from wet chemical method.

Wet chemical synthesis methods allow us to achieving preferred size, shape, phase, surface structure of oxide nanoparticles leading to desired properties for possible applications[8]. The wet chemical synthesis of metal oxide nanoparticles has great control over the quality of nanomaterials. Samapti et.al have prepared ZnO nanorods [9], Yan et. al have prepared CeO2 nanopartcles [10], Li et al have prepared Co3O4 [11]by wet chemical method. They were taken Zn metal powder, sodium hydroxide (NaOH) pellets and ammonium peroxodisulphate as precursors.

Top-down approach rather initiate with macroscopic structures, controlling externally the process of formation of nanostructures. Mechanochemistry is concerned with the chemical reactions and structural deformations induced by the applied mechanical energy [12]. Mechanical alloying is an effective and popular modern age Top-down method of nanomaterial synthesis. It is generally carried out 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 powder 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], Mn-doped CeO2 nanomaterials [14] by the Mechanical alloying. The XRD patterns of unmilled ZnO and all ball milled Mn doped ZnO sample with different milling times are shown in Fig.1.

C:\Users\Arup\Desktop\XRD planes PS N.tif

Fig.1: Indexed XRD patterns of unmilled (0h) and ball milled Mn doped ZnO nanocrystallites.

**Electrical transport properties of oxide nanomaterials:**

It is very much essential to realize the electrical properties of nanostructured materials for different applications especially in electronics. The properties of any material is associated with its the atomic structure and electromagnetic structure i.e the energy density distribution of the material. The outermost electrons of the atoms take part in the electrical conduction phenomena. The electrical properties of nanomaterial depend on the composition, shape, size and charge concentration of the particles [15,16]. By controlling the charge carrier density one can control the electrical properties of the nanomaterial. The electrical and dielectric properties of nanostrutured 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 materials can exhibit ionic and electronic or mixed ionic/electronic conduction influenced by the nanostructure, doping element, stoichiometry and presence of disorder in the material. The number of electronic charge carriers in a metal oxide is a function of the band gap energy according to the Boltzmann statistics. [Electrical conductivity](https://www.sciencedirect.com/topics/engineering/electrical-conductivity) is the movement of charge in response to an electric field. In the familiar solid conductors, i.e. metals and semiconductors, the charge movement, or current, is due to electrons or holes and is described as [electronic conductivity](https://www.sciencedirect.com/topics/engineering/electronic-conductivity). The electronic conduction is referred to as n or p hopping-type depending on whether the principal charge carrier are electrons or holes respectively. Hopping refers to tunneling transitions from occupied to unoccupied localized states, the state energy difference being bridged by emission or absorption of one or several phonons. The number of “free” electron/holes of an oxide can be enhanced by introducing non-stoichiometry and, in such case, are balanced by the much less mobile oxygen/cation vacancies. According to Godet variable range hopping theory (3D G-VRH) [18,19], the temperature dependence of for the three dimensional materials can be expressed as,

(T) = exp ()1/4 (1)

where is a constant and T0 is the Godet characteristic temperature. The average hopping distance (R) which depends on the density of state (DOS) and their distribution. The hopping energy (W) depends on the average hopping distance (R)[20,21]. The average hopping distance and the activation energy are decreases with reduction of crystallite size. The prediction of the modeling is justified in case of Mn doped ZnO nanocrystallites by the linear relationship between ln andor exponential relation between and in Fig 2.

C:\Users\Arup\Desktop\sigma 00 tiffps.tif

Fig.2: Variations of (vs T-1/4) and (lnvs T-1/4) (inset) for Mn doped ZnO nanocrystals

In the low temperature region temperature dependent dc conductivity (T) is mainly attributed by the intrinsic nature of the sample because the number of charge carriers and mobility of the charge carriers are appreciably low at this region. But the number of charge carriers as well as mobility increases from the defects level due to thermal excitation in the high temperature region. In disordered semiconductors, low temperature electrical transport occurs via localized electronic states near a so-called ‘transport level’ which depends on the shape of the density of state (DOS), position of the Fermi level and temperature. In ZnO nanocrystal, at temperature higher than room temperature both zinc interstitial (Zni) and oxygen vacancies (Vo) are major defects and act as donor in ZnO and transfer excited electrons from donor level to the conduction band, consequently enhances conductivity. The frequency dependent real part of the ac conductivity ( of the Mn-doped ceria samples is calculated using the equation ( = tan at different temperatures [22] are shown Fig.3.

C:\Users\Administrator\Desktop\log sigma at CM8ps.tif

Fig.3: Variation of the real part of the ac conductivity (of Mn-doped CeO2 nanocrystals at different temperatures

In an analogous manner to hoping-type conduction, ionic conduction takes place when ions can hop from site to site within a crystal lattice as a result of thermal activation, and is typically interpreted on the basis of a modified Fick´s second law. Ionic [conductivity](https://www.sciencedirect.com/topics/chemistry/conductivity) is electrical conductivity due to the motion of ionic charge. Fundamental science introduces the ionic conduction as a property of liquid [electrolyte solutions](https://www.sciencedirect.com/topics/chemistry/electrolyte-solution). 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, like electronic conductivity, can be expressed as a product of three terms: the carrier charge (q), the concentration (number of particles per unit volume, n) and the mobility (the [average velocity](https://www.sciencedirect.com/topics/engineering/average-velocity) of a carrier due to an [applied electric field](https://www.sciencedirect.com/topics/engineering/applied-electric-field) of unit strength, b). Thus we may write an expression for the specific conductivity as

In the case of ionic conductivity, many different carriers may be encountered, but [ionic mobility](https://www.sciencedirect.com/topics/chemistry/ionic-mobility) is generally much smaller than the values typically found for electrons.

**Summary and Prospects:**

In the last few decades, the research and development of different methods of processing to synthesize metal-oxide nanoparticles have made significant progress. A variety of metal-oxide nanoparticles including doped oxides and complex 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, A 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.