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Enhancement of ionic conductivity in Li_2O–SiO_2 glass in nanodimensions grown within pellets of ZnO nanorods and magnetodielectric properties of these nanocomposites

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ABSTRACT

$23Li_2O \cdot 77SiO_2$ glass with nanodimensions was grown within the pores of a pellet formed by ZnO nanorods of a diameter of 70 nm and lengths varying from 80 nm to 270 nm. The resistivity of the nanoglass was less than that of its bulk counterpart by more than three orders of magnitude. The activation energy was found to be 35% lower than that of the bulk glass. This was ascribed to an increase in free volume in the nanodimensional glass. The ac conductivity variation at high frequency showed an exponent of 0.5 indicating two dimensional movements of lithium ions in the nanoglass. Nanocomposites of lithia–silica nanoglass and CuO nanoparticles showed magnetodielectric property with dielectric permittivity at 500 kHz decreasing by 5.3% at 2 T. This was explained on the basis of space charge polarization and Hall Effect. Nanocomposites of lithia–silica nanoglass and ZnO nanorods exhibited a giant magnetodielectric effect with the dielectric permittivity increasing by 20% to 99% at 2 T depending on the measuring frequency. This was also ascribed to space charge polarization with the ZnO nanophase showing a negative magnetoresistance.

1. Introduction

Nanodimensional glasses have attracted considerable attention in recent years because of unusual properties exhibited by them [1–4]. Most of the work reported so far was concerned with assemblies of nanoparticles of metals or metallic glasses [5]. The inert gas evaporation technique was used for the synthesis of such particles [6]. The structure of these nanoglasses has been explained on the basis of the incoherent interfaces generated by the nanocrystallites. A delocalization of the interfaces could be brought about by suitable heat treatment. This helped to bring about spreading of free volume at the interface throughout the glass structure [7,8]. Though the work on nanoglasses has so far been restricted mostly to metallic systems, some attempts have been made to create a disordered atomic configuration at the interfaces between nano core–shell structures e.g., copper–copper oxide [9] and iron–iron oxide [10]. Conductivity enhancement by seven to eight orders of magnitude was observed in these nanocomposites with respect to that of a silicate glass containing an equivalent amount of transition metal ions concerned. A small polaron hopping conduction mechanism was shown to be operative in these systems and the activation energy was reduced due to the concentration of copper and iron ions respectively within the restricted volume of the interface [9,10]. This caused an increase in the value of the effective dielectric constant of the region concerned resulting in a reduction of the activation energy.

Nanodimensional lithia–silica glasses have recently been synthesized within the pores of a pellet comprising CuO nanoparticles [11]. The glass layers around CuO nanoparticles of a diameter of 17 nm were shown to have a thickness around 5 nm. The resistivity of the

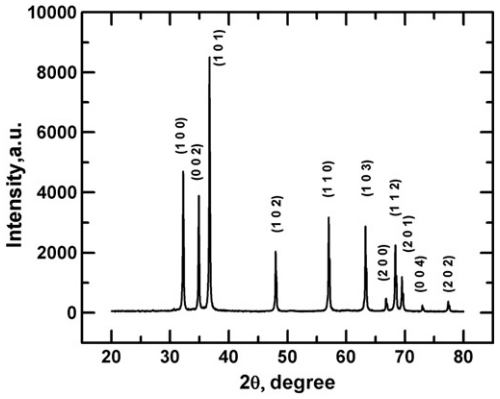

Fig. 1. X-ray diffractogram of ZnO nanorods.

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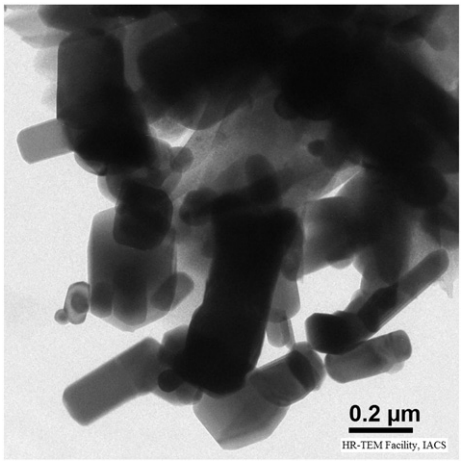

Fig. 2. Transmission electron micrograph of ZnO powder (Loba Chemie).

nanoglass was found to be about four orders of magnitude smaller than that of the corresponding bulk glass. Such changes arose due to a reduction in the activation energy of the lithium ion conduction in the nanoglass. This was explained as being caused by an increase in free volume of nanoglass. We have now explored the use of ZnO nanorods as template for growing lithia–silica nanoglass. ZnO has a hexagonal Wurtzite structure and it has been shown earlier that they can be grown in the form of nanowires/nanorods [12]. Such one-dimensional nano-structural growth of ZnO has been exploited by earlier researchers to generate useful physical properties in them e.g., photodetection [13]. The large numbers of surface defects present in them have been responsible for this behavior. Photoluminescence studies on the grown ZnO nanorods have been carried out [14,15]. We have prepared nanoglass in lithia–silica system using ZnO nanorod compact as the template. Our motivation was to ensure the growth of a continuous silica nanoglass on the surfaces of ZnO nanorods present within the polycrystalline compact. The ionic conductivity was found to be higher than that of the corresponding bulk glass. Silica-based glasses grown within the above mentioned semiconducting oxide templates provide an ideal opportunity to test the magnetocapacitance effect in a non magnetic composite structure as recently predicted theoretically [16]. We have used nanocomposites comprised of silica-based nanoglasses and both nanostructured CuO and ZnO templates respectively. Indeed, we observed reasonably high magnetocapacitance effect in these systems. The details are reported in this paper.

Table 1
Comparison of d_{hkl} values obtained from electron diffraction with ASTM data for ZnO.

Crystal planes	Measured d_{hkl} spacings (nm)	ASTM d_{hkl} spacings (nm)
0001	0.53	0.52
0100	0.28	0.28
0101	0.25	0.25
0002	0.26	0.26

2. Experimental

ZnO powders supplied by Lobachemie were subjected to mechanical attrition by mounting them in a Pulverisette Planetary ball mill (Germany) with grinding media zirconia spheres having a diameter of 0.5 cm dispersed in ethanol contained in a zirconia bowl with a capacity of 45 ml for 5 h. The resulting powder was dried at 333 K in an electrical oven for 12 h. The X-ray diffraction pattern of the powder was recorded in a Bruker D8 XRD SWAX diffractometer using Cu K_α radiation to confirm the presence of ZnO. The crystallite size of ZnO was estimated from the line widths of the diffraction peaks by using Scherrer equation [17]. The value was 66 nm. Pellets of 1 cm diameter were prepared by taking the powder in a mould with a diameter of 1 cm and subjecting the same to a load of 5 t. These were subjected to a heat treatment at 423 K for 5 h.

A sol with a target glass composition $30Li_2O \cdot 70SiO_2$ was prepared taking lithium nitrate and tetra ethyl ortho silicate as the precursors. A solution containing 1 ml of tetra ethyl ortho silicate (TEOS) in 2 ml of ethyl alcohol was prepared. Another solution was made by dissolving 0.261 g $LiNO_3$ in 2 ml ethanol. The two solutions were mixed and stirred for 5 h. The heat treated ZnO pellets described previously were then dipped into the sols described above for a period of 30 h. After taking out the pellets from the sol and cleaning both of the faces with ethyl alcohol the pellets were dried at room temperature for two days. They were then heated at 673 K for $1\frac{1}{2}$ h. Bulk glass of target composition $30Li_2O \cdot 70SiO_2$ was prepared by a sol–gel process as reported earlier [11]. X-ray photoelectron spectroscopy was used to determine the actual composition of the glass prepared. This was found to be $23Li_2O \cdot 77SiO_2$. The details have been given earlier [11].

The microstructure of the composites was studied by a JEOL 2010 high resolution transmission electron microscope. A field emission scanning electron microscope (JEOL JSM-6700F) was used to estimate the areal fraction of the nanoglass phase in the composite.

Electrical measurements on the composites were carried out after coating both faces of the pellets with silver paint electrodes (supplied by M/S Acheson Colloiden B.V., Netherlands). Fine copper wires were

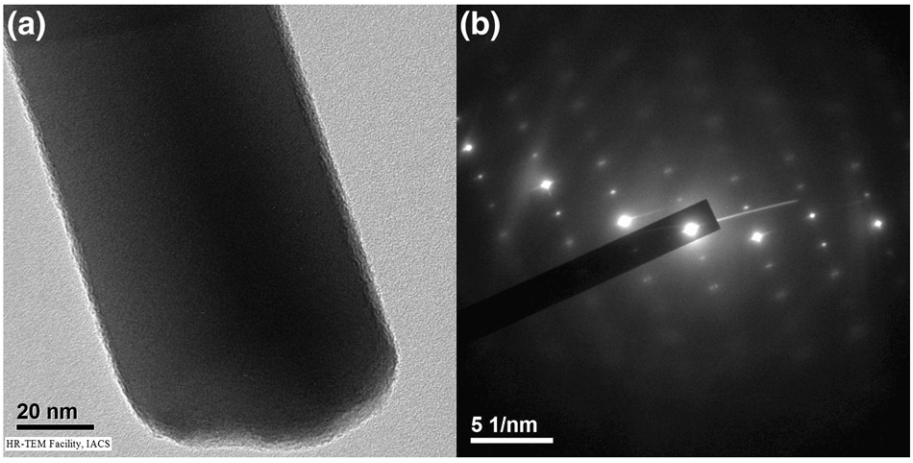

Fig. 3. (a) Transmission electron micrograph of typical ZnO nanorod after milling. (b) Electron diffraction of Fig. 3(a).