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SYNTHESIS AND CHARACTERISATION OF SEMICONDUCTOR OXIDE $MgIn_2O_4$ POWDER

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$MgIn_2O_4$ having the spinel structure was prepared by oxalic acid precursor route and the electrical, thermal and optical properties were measured. $MgIn_2O_4$ spinel was found to be a promising material as a transparent electronic conductor. By the measurements of diffuse reflectance spectra, $MgIn_2O_4$ was found to have a wider band gap (~3.3 eV) than indium tin oxide (ITO). The resistivity of the sintered sample of $MgIn_2O_4$ in air was 7.14 x 10^2 ohm-cm and in $N_2 - H_2$ mixture was 7.81 x 10^0 ohm-cm.

Keywords: Semiconductors, magnesium indate, spinel

INTRODUCTION

Most of p-block metal oxides such as SiO_2 and Al_2O_3 are electrical insulators because of their wider band gap. The wide-gap characteristic derives from the fact that the energy level of O 2p, which constitutes the upper edge of a valence band, is very deep with respect to the vacuum level, or in other words, cation-oxygen bonding has a considerable ionic character. The optical band gap varied from about 1.0 eV in Tl_2O_3 to about 9.0 eV in SiO_2 exhibiting a conduction type variation from metallic to insulating. Out of these materials, the oxides of the fourth and fifth row elements in the periodic table have wider band gaps greater than 3 eV. ZnO, In_2O_3 and SnO_2 are some of the technologically important materials because they have the specific properties of metallic conduction retaining the transparency to the visible light. Typically indium oxide, In_2O_3 doped with tin Sn (ITO) is widely studied and used for various applications such as transparent contacts for liquid crystal display (LCD) and solar cell and as heat reflector glass [1]. Though the above oxides have high transparency and conductivity, they are often limited in their applications. The reason is that they are unstable chemically and thermally when used in various environments. Most of their problems are caused by their intrinsic properties and the method used for the preparation. Recently, excellent optical properties and chemical stability have been attained with new materials, such as impurity-doped $InGaO_3$ [2,3] or undoped $ZnSnO_3$ [4], respectively. In addition, transparent conducting films have been recently prepared with new materials, such as Zn_2SnO_4 [5,6], yttrium-doped $CdSb_2O_6$ [7] and $MgIn_2O_4$ [8]. However, the resistivities obtained for these transparent conducting oxide films were only 10^{-2} to 10^{-3} ohm-cm.

In this context, search for new semiconductor oxides is continuing which are generally stable at elevated temperatures under oxidising conditions. Magnesium indate ($MgIn_2O_4$), a semiconductor oxide is one of such materials. It has been synthesised through the oxalic acid precursor route for the first time. Electrical, optical and thermal studies were conducted on the $MgIn_2O_4$ pellet and the results are presented in this paper.

EXPERIMENTAL

Polycrystalline samples of magnesium indate has been prepared by dissolving stoichiometric mixture of basic magnesium carbonate ($MgCO_3$) and indium oxide (In_2O_3) salts in 1 *M* of oxalic acid. The resulting solution was dried at about 333-343 K to get a dry mass and ground well in an agate mortar for homogeneity. The powdered samples were calcined at 1173 K for 24 h and made into pellets of 12 mm dia and 2 mm thickness in a Peeco hydraulic press at a pressure of 2 tonnes/cm^2. The pellets were sintered at higher temperatures ranging from 1273 to 1573 K for the duration of 24 to 60 h. The crystal structures of the samples were

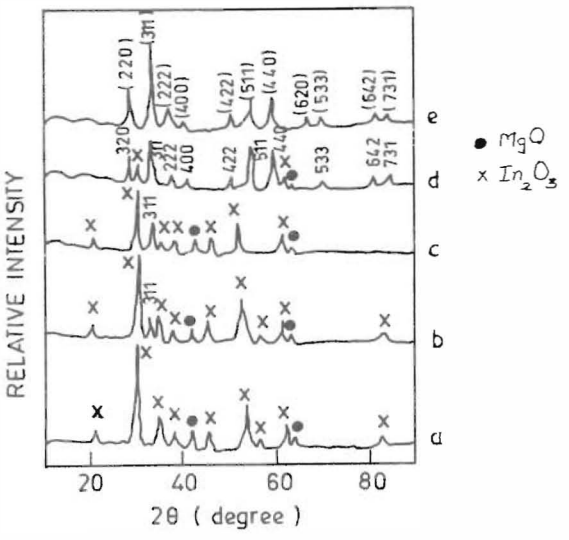

Fig. 1: X-ray diffraction patterns of ($MgCO_3 : In_2O_3 : (COOH)_2 . 2H_2O$) powder heated at (a) 1173 K for 24 h (b) 1273 K for 24 h (c) 1373 K for 24 h (d) 1473 K for 48 h (e) 1573 K for 60 h

identified by powder X-ray diffraction (XRD) with CuK_α radiation.

The dc electrical conductivity of the pellet was measured by two probe technique. To study the thermal stability of the pellet, the variation of resistance with temperature was measured. The diffuse reflectance spectra were taken using Hitachi U3400 UV-VIS-NIR spectrophotometer in the wavelength range of 350-600 nm. The spectrum of the standard In_2O_3 powder was also taken for comparison.

RESULTS AND DISCUSSION

Powder X-ray diffraction patterns of the samples heated at different temperatures were obtained under high gain in order to detect possible formation of the second phase is shown in Fig. 1. Sample heated at 1173 K for 24 h, corresponds to MgO and In_2O_3 peaks thereby showing no phase formation of $MgIn_2O_4$. $MgIn_2O_4$ formation was initiated at 1273 K. Monophase of $MgIn_2O_4$ was formed on heating at 1573 K,

TABLE I

Temperature K	% of MgO	% of In_2O_3	% of $MgIn_2O_4$
1173	13.36	89.64	-----
1273	10.08	75.72	14.20
1373	8.27	60.46	31.27
1473	4.14	35.12	60.74
1573	-----	-----	100.00

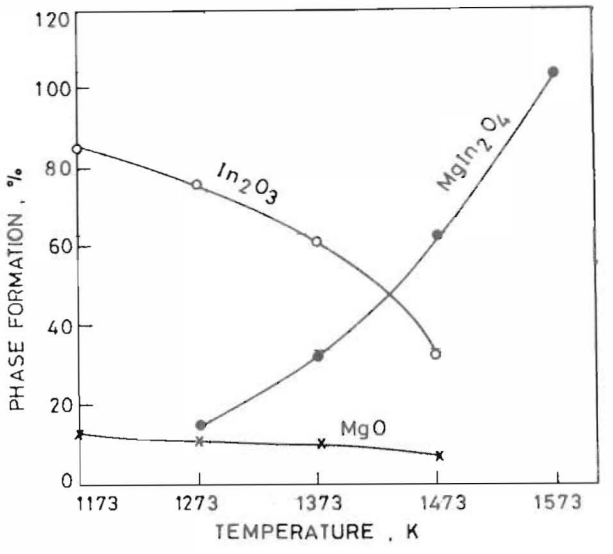

Fig. 2: Percentage of MgO, In_2O_3 and $MgIn_2O_4$ at different temperatures

60 h with spinel cubic structure. The percentage of phase formation is tabulated in Table I and is shown in Fig. 2.

The dc electrical resistivity of the pellet sintered at 1573 K for 60 h is 7.14 x 10^2 ohm-cm. In order to decrease the resistivity, the pellet was sintered at 673 K and 773 K in $N_2 - H_2$ mixture. The resistivity was decreased and is 7.81 x 10^0 ohm- cm. The variation of resistance with time

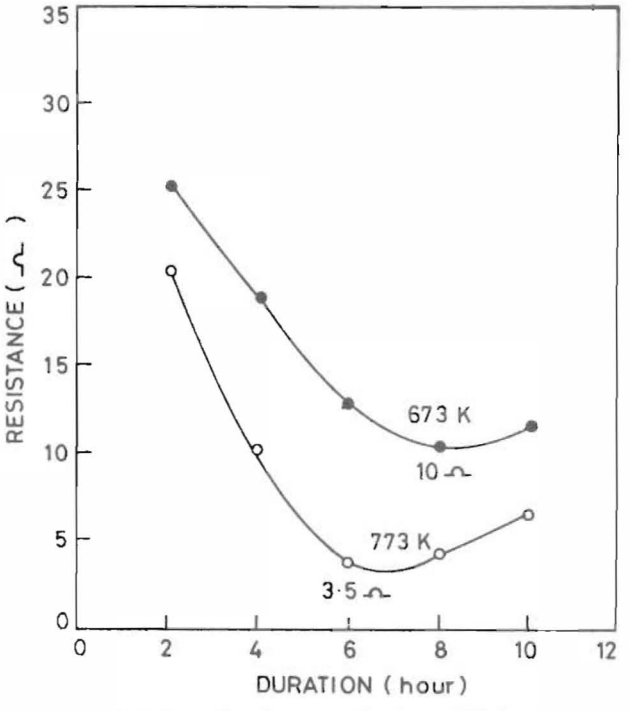

Fig. 3: Variation of resistance with time of $MgIn_2O_4$ pellet sintered in N_2–H_2 mixture at different temperatures

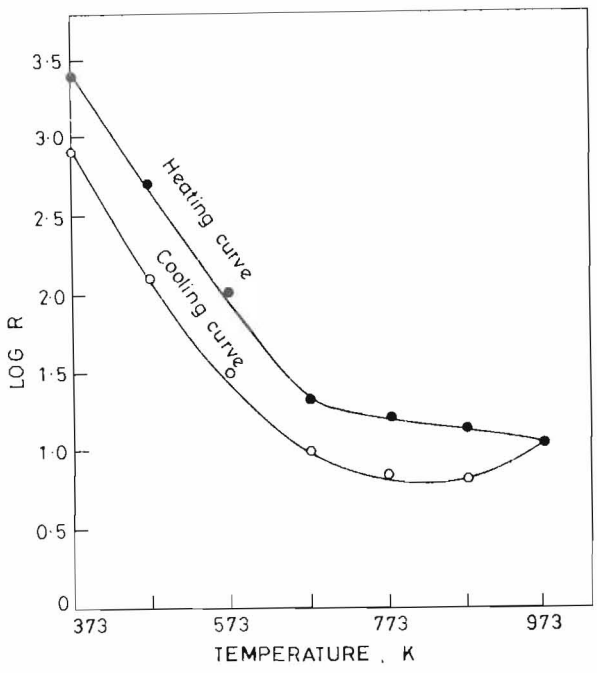

Fig. 4: Resistance versus temperature of $MgIn_2O_4$ pellet sintered in air

heated at 673 K and 773 K in $N_2 - H_2$ mixture is shown in Fig 3.

To study the thermal stability of the pellet, the variation of resistance with temperature was studied upto about 973 K in air. Log R vs temperature was plotted and is shown in Fig. 4. Both the heating and cooling curves have the same slope. This indicates that $MgIn_2O_4$ has good thermal stability in oxidizing atmosphere at elevated temperatures. A decrease in resistance with increasing temperature shows that $MgIn_2O_4$ has semiconductor behaviour. So we conclude that $MgIn_2O_4$ is a semiconductor oxide material.

From the diffuse reflectance spectra shown in Fig. 5, we conclude that the reflectance value of $MgIn_2O_4$ is reduced above 450 nm when compared to the standard In_2O_3 spectrum which was caused by conduction electrons. It is assumed that the concentration of conduction electron is increased in the case of $MgIn_2O_4$. So we conclude that $MgIn_2O_4$ has higher conductivity than standard In_2O_3 powder. The absorption edge of $MgIn_2O_4$ appears near 381 nm and is shorter wavelength than that of In_2O_3. This observation shows that the bandgap of $MgIn_2O_4$ is much higher than that of the In_2O_3.

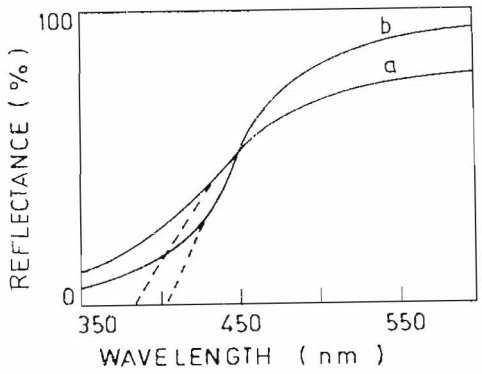

Fig. 5: Diffuse reflectance spectra of (a) $MgIn_2O_4$ and (b) In_2O_3 powder

CONCLUSION

$MgIn_2O_4$ has been synthesised by oxalate precursor route. The structure was observed to be cubic spinel. The dc electrical resistivity of $MgIn_2O_4$ in air is 7.14×10^2 ohm-cm. In $N_2 - H_2$ mixture, the resistivity is decreased to 7.81 ohm-cm. By the measurements of diffuse reflectance spectra, the optical bandgap of $MgIn_2O_4$ (~3.3 eV) was found to be wider than that of In_2O_3. Variation of resistance with temperature graph indicates that $MgIn_2O_4$ has good thermal stability in oxidising atmosphere at elevated temperatures.

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