

Combustion synthesis of magnesium indate, MgIn_2O_4

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Abstract

MgIn_2O_4 , a mixed oxide with spinel structure was prepared by combustion synthesis using metal nitrates and urea as fuel. Structural, optical and electrical characterization of the same was carried out. From the diffuse reflectance spectral measurement of MgIn_2O_4 , the band gap was found to be 4.3 eV which is higher than that of indium tin oxide (ITO). The conductivity of as prepared sample and that of the H_2 -annealed sample of MgIn_2O_4 was 1.56×10^{-3} and $5.57 \times 10^0 \text{ S cm}^{-1}$. The particle size of the above combustion derived sample was found to be 2–3 μm . © 2001 Published by Elsevier Science B.V.

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1. Introduction

Advanced ceramics or fine ceramics are high value-added inorganic materials produced from high purity synthetic powders to control microstructure and properties. Wet-chemical routes [1], e.g. co-precipitation, sol–gel, spray-dry, freeze-dry, etc., are usually employed to prepare advanced ceramic powders having submicron size, narrow size distribution and absence of particle agglomerates. However, these methods usually involve long processing time, costly chemicals and sophisticated equipments, besides high operation temperature. Hence, the need for an alternative to the wet-chemical methods was felt.

Many attempts have been made to use the heat generated by exothermic chemical reactions in the synthesis of high-temperature ceramic materials [2]. This process, popularly known as self-propagating high-temperature synthesis (SHS), is also called Furnaceless or fire synthesis or combustion synthesis (CS). In recent years, CS technique has attracted a good deal of attention due to the production of homogeneous, very fine unagglomerated multicomponent oxide ceramic powders without intermediate decomposition and/or calcination steps [3]. In CS technique, an aqueous solution containing corresponding metal nitrates (oxidizers) and a suitable organic fuel (reducer), taken in stoichiometric ratio, is allowed to boil, till the mixture is ignited and thus resulting in self-sustaining fast combustion reaction which produces fine crystalline oxide powders. In the above

process, the energy released from the exothermic reaction between the nitrates and the fuel, which is usually ignited at a temperature much lower than the actual phase transformation temperature, can rapidly heat the system to a high temperature and sustain it long enough, even in the absence of an external heat source.

With a view to develop photoelectronic devices with higher functions, synthesis of magnesium indate (MgIn_2O_4), a spinel oxide having higher transparency and higher conductivity, has been attempted by CS technique. As per the literature survey hitherto it has been prepared by solid state reaction [4] only. Details of synthesis of MgIn_2O_4 by CS, its structural, electrical, optical and physical characterization are reported in this short communication.

2. Experimental

Redox mixtures for CS of MgIn_2O_4 were prepared by mixing stoichiometric amounts of magnesium nitrate, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and indium nitrate, $\text{In}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ (oxidizers) with urea, H_2NCONH_2 (fuel). The oxidizers to fuel ratio plays an important role in the CS as it determines the exothermicity of the reaction which in turn affects the surface area and particle size of the product. The stoichiometry of the redox mixture used for the combustion reaction was calculated based on the total oxidizing (O) and reducing (F) valencies of the components which serve as numerical coefficients for stoichiometric balance.

The energy released during the combustion is maximum, when the equivalence ratio ϕ_e , i.e. the ratio of the oxidizing

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valency of metal nitrates to the reducing valency of fuel is one ($\phi_e = O/F = 1$) [5]. According to the concepts used in propellant chemistry, trivalent, divalent metals and elements like C, H, O have valencies +3, +2 and +4, +1, –2, respectively. Nitrogen is considered to have a valency of zero because of its conversion to molecular nitrogen during combustion. Accordingly, the oxidizing valency (O) of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is –10 and $\text{In}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ is –15 and the reducing valency (F) of H_2NCONH_2 is +6. In the present investigation, for one mole of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and two moles of $\text{In}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$, the amount of urea required is calculated using the general empirical formula for the system

$$1(-10) + 2(-15) + n(+6) = 0, \quad n = 6.67 \text{ mol}$$

For experimental work, four different conditions with four different mole concentrations of urea, viz., 6, 6.67, 7 and 8 mol were used for the preparation. Single phase MgIn_2O_4 formed, when 7 mol of urea was added.

Preparation of MgIn_2O_4 by CS is given in the form of flow chart in Fig. 1. The aqueous solution containing stoichiometric amount of redox mixture was taken in a cylindrical pyrex dish of approximately 200 ml capacity and rapidly heated the solution in a muffle furnace, preheated to 500°C . The solution initially undergoes dehydration followed by foaming. It then burns giving a fluffy mass of oxide materials. Metal nitrates and urea decompose at the ignition temperature releasing a mixture of combustible gases [6]. The resultant fluffy mass was ground well in an agate mortar, calcined at 700°C for 24 h and again ground well by ball milling for half-an-hour. The finely powdered samples were mixed with polyvinyl alcohol as binder (5 wt.% aqueous solution), in the ratio 20:1 and were made into pellets of 12-mm diameter and 2-mm thickness by applying a pressure of 2 ton cm^{-2} using a PEECO hydraulic press. The binder was removed by heating slowly to 300°C . The pellets and also the powders were sintered at different temperatures ranging from 800 to 1200°C for different duration 12–60 h. The bulk and the powder densities were measured using Archimede's liquid displacement technique [7].

Powder X-ray diffraction patterns were recorded in a JEOL JDX-8030 X-ray diffractometer with $\text{Cu K}\alpha$ radiation in the 2θ range 10 – 85° with Ni filter. Lattice parameter ' a ' was computed from 2θ values using a least square refinement program. KBr was used as the internal standard for correcting the instrumental errors. Particle size of the sample was analysed using a Malvern Laser Particle size Analyser 3.0. The diffuse reflectance spectra were recorded using a Hitachi U-3400 UV–Vis–NIR Spectrophotometer with alumina as standard in the wavelength region 200–800 nm. TG and DTG traces were recorded simultaneously in the temperature range 30 – 1000°C using STA 1500 Simultaneous Thermal Analysis System of Rheometric Scientific.

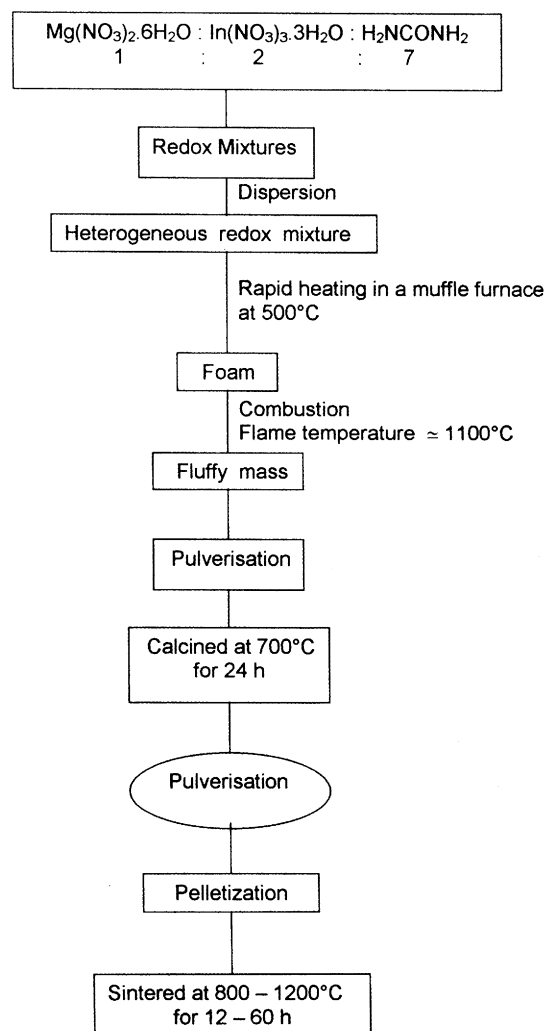


Fig. 1. Flow chart for the preparation of MgIn_2O_4 compound by CS technique.

3. Results and discussion

TG and DTG traces of as-prepared combustion powder of MgIn_2O_4 are shown in Fig. 2. The DTG pattern shows two strong peaks observed near 76°C and 123°C and a weak peak observed near 597°C . The peak at 76°C is due to the dehydration of residual moisture of the sample during loading and the peak at 123°C is attributed to the decomposition of urea. The weak peak at 597°C is mainly attributed to the decomposition of magnesium nitrate. This is substantiated further by the two step weight losses observed in the TG curve in the temperature ranges 63 – 77°C and 100 – 126°C , which may be attributed to the removal of moisture and decomposition of urea, respectively. Further, the weight loss corresponding to the decomposition of magnesium nitrate is observed in the temperature range 540 – 604°C . There is no evidence for compound formation in TG and DTG experimental results. This clearly shows that the compound formation occurs above 1000°C .

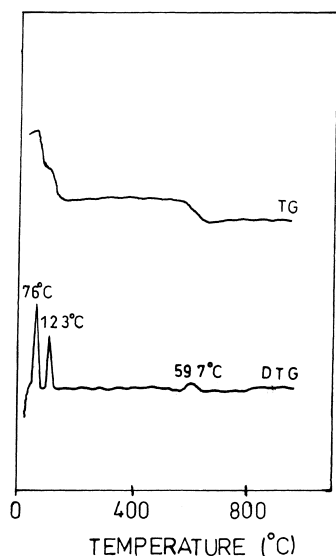


Fig. 2. TG and DTG traces of as-prepared combustion derived powder of MgIn_2O_4 .

Fig. 3 gives the powder X-ray diffraction patterns of as-prepared combustion derived powder of MgIn_2O_4 , sintered at different temperatures for 48 h. MgIn_2O_4 phase formation is initiated at 900°C , which increases with increasing temperature, but MgO and In_2O_3 phases decrease

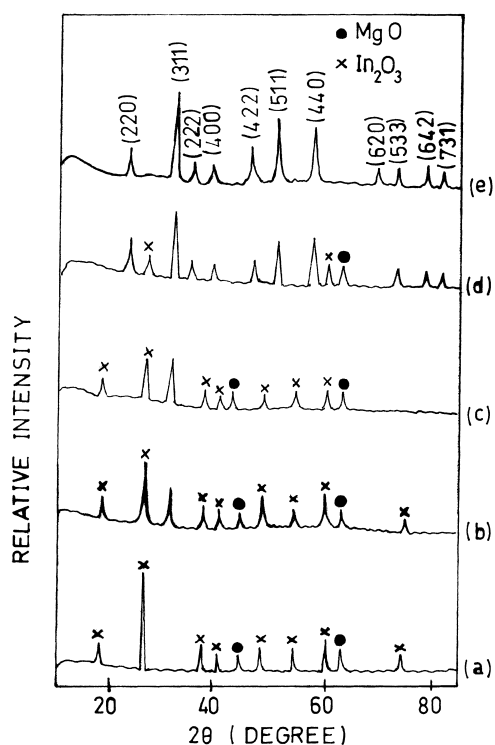


Fig. 3. Powder X-ray diffraction patterns of as-prepared combustion derived powder of MgIn_2O_4 , sintered at different temperatures for 48 h: (a) 800°C ; (b) 900°C ; (c) 1000°C ; (d) 1100°C ; (e) 1200°C .

Table 1

Percentage of MgO , In_2O_3 and MgIn_2O_4 phases formed in the sample heated at different temperatures for 48 h

Temperature ($^\circ\text{C}$)	Phase formation (%)		
	MgO	In_2O_3	MgIn_2O_4
800	35.13	64.87	—
900	22.02	56.62	21.36
1000	10.87	40.16	48.97
1100	5.01	23.62	71.37
1200	—	—	100.00

with increasing temperature. Single phase MgIn_2O_4 is formed, when the sample is heated at 1200°C for 48 h. Beyond 48 h the intensity of the peaks corresponding to MgIn_2O_4 decreases with the formation of secondary phases as evidenced from the XRD. These secondary phases are due to the decomposition of the compound. A comparison with the standard values of JCPDS, the plane of each peak at 1200°C for 48 h heating confirms that the sample possesses a cubic spinel structure.

The percentage of phase formation is summarized in Table 1. The phase formation is estimated from the relation [8],

$$\text{percentage of } \text{MgIn}_2\text{O}_4 = \frac{I_{\text{MIO}}}{I_{\text{MIO}} + I_{\text{MO}} + I_{\text{IO}}} \times 100$$

where I_{MIO} is the maximum intensity of MgIn_2O_4 peak, I_{MO} the maximum intensity of MgO peak, and I_{IO} the maximum intensity of In_2O_3 peak.

The diffuse reflectance spectra of MgIn_2O_4 and standard indium tin oxide (ITO) powder are shown in Fig. 4. The fundamental absorption edge of MgIn_2O_4 appears near 288 nm, which is a shorter wavelength than ITO [9]. From this the

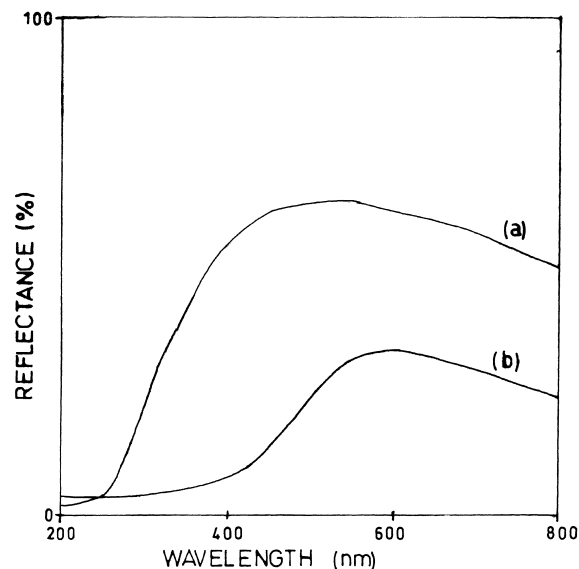


Fig. 4. Diffuse reflectance spectra of (a) MgIn_2O_4 and (b) ITO powder.

optical band gap E_g was calculated using the relation:

$$E_g = \frac{1.24}{\lambda_{\max}}$$

where $\lambda_{\max}$ is the fundamental absorption edge of the material in μm . The optical band gap of MgIn_2O_4 is found to be 4.3 eV, which is greater than that of MgIn_2O_4 synthesized by the ceramic method (3.4 eV) [4] and standard ITO (2.9 eV). The variation in bandgap may be attributed to the variation in particle size. The optical transmittance of MgIn_2O_4 synthesized by CS is much higher than that of ITO in the blue region (400–500 nm), which is important for application in full coloured LCDs. The band gap of MgIn_2O_4 synthesized by CS being greater than 4 eV makes it a very good transparent conducting oxide material.

The foam and the tap densities of the as-prepared combustion powder, and the green density of the pellet (before sintering) were measured. The powder density of the sintered sample was measured and is 95% of theoretical density (6.065 g cm^{-3}). From the particle size measurements, it is observed that 75% of particles have size 2–3 μm

and the specific surface area of MgIn_2O_4 is $0.31 \text{ m}^2 \text{ g}^{-1}$. The type of material was ascertained by the hot probe method to be n-type.

MgIn_2O_4 pellets, sintered at different temperatures ranging from 900 to 1200°C in steps of 100°C for different durations from 12 to 60 h in air. The conductivity of each sample was measured by the two probe method (Fig. 5(a)). From the figure, it is seen that at all temperatures, the conductivity increases with increasing sintering time upto 36 h and then decreases. Higher conductivity is obtained when the pellet is heated at 1200°C for 36 h which corresponds to $1.56 \times 10^{-3} \text{ S cm}^{-1}$. With a view to increasing the conductivity, the pellets sintered at the optimized conditions for maximum conductivity were chosen for further work. Thus, MgIn_2O_4 pellets sintered at 1200°C for 36 h were further subjected to post heating cum annealing treatment at various atmospheres like N_2 and H_2 at different temperatures for different duration. The results are graphically shown in Fig. 5(b) and (c).

Fig. 5(b) shows the variation of conductivity with sintering time of MgIn_2O_4 pellets, post heat treated at different

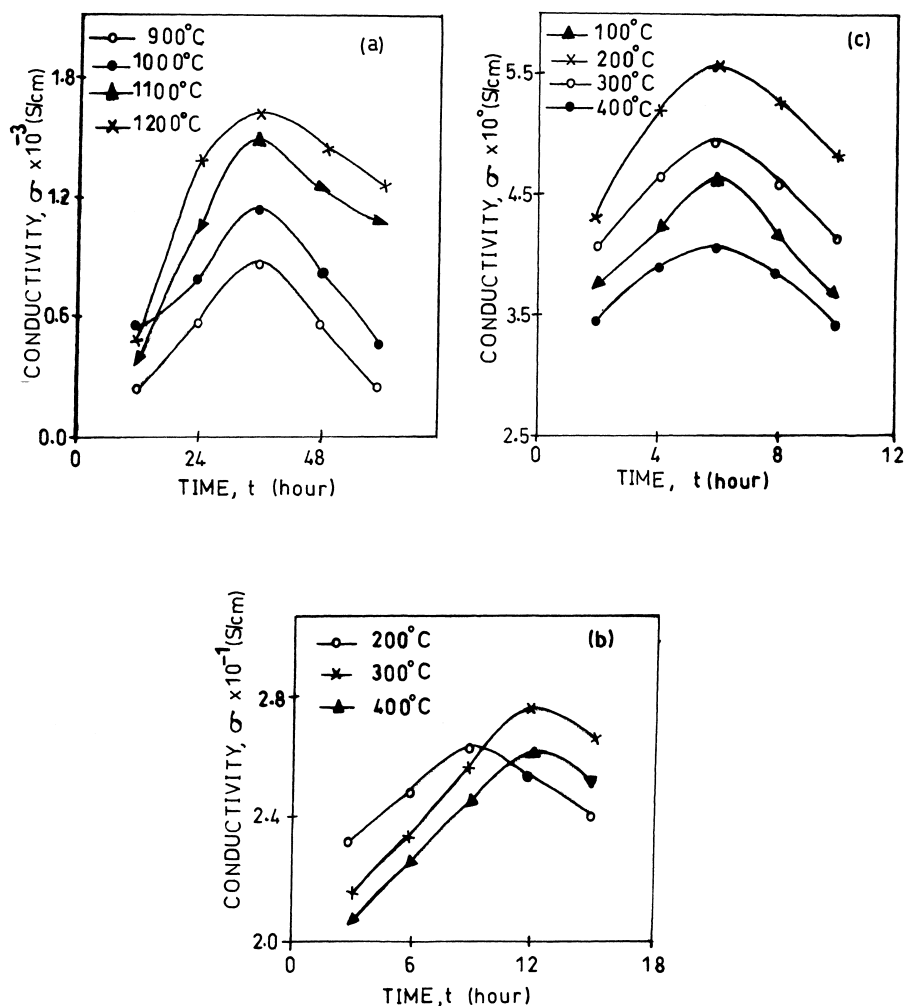


Fig. 5. $\sigma - t$ plots for MgIn_2O_4 pellets heated in (a) air, (b) N_2 atmosphere and (c) H_2 atmosphere.

Table 2
Optimized conditions to obtain maximum conductivity of combustion derived MgIn_2O_4 compound

Atmosphere	Temperature ($^{\circ}\text{C}$)	Duration (h)	Conductivity, σ (S cm^{-1})
Air	1200	36	1.56×10^{-3}
N_2	300	12	2.75×10^{-1}
H_2	200	6	5.57×10^0

temperatures ranging from 200 to 400°C for different duration in N_2 atmosphere. At 200°C , the conductivity increases with increasing temperature upto 9 h of duration and then decreases. But, at 300 and 400°C , the conductivity increases upto 12 h and then decreases. Highest conductivity is obtained when the pellet is heated at 300°C for 12 h and the value is $2.75 \times 10^{-1} \text{ S cm}^{-1}$. Fig. 5(c) shows the variation of the conductivity of MgIn_2O_4 pellets post heat treated in H_2 atmosphere, at different temperatures ranging from 100 to 400°C . Here also the trend is the same as in previous cases, highest conductivity being obtained at 200°C for 6 h heating and its value is $5.57 \times 10^0 \text{ S cm}^{-1}$. From the figures, it is observed that at all temperatures in various atmospheres, the conductivity increases with increasing heating time and then decreases. Table 2 indicates the optimised conditions to obtain maximum conductivity of combustion derived MgIn_2O_4 compound at various atmospheres. In the case of hydrogen atmosphere, due to the production of oxygen vacancies, the conductivity increases. In air, the pellets show lesser conductivity value, showing that the oxygen vacancies are not created. But in the N_2 atmosphere (commercial), the conductivity increases with heating time and the conductivity values are higher than that of the pellets heated in air.

In general, conduction electrons in the n-type oxide semiconductors are generated from interstitial or substituted cations or oxygen vacancies. In the present study, conductivity of the sample which was annealed in the oxidizing atmosphere, air decreased, whereas enhancement of conductivity has been observed when the sample was annealed in the reducing atmospheres. These observations indicate that the changes in the conductivities due to the heat treatment under different ambient were caused by the changes in the concentration of the conduction electrons that were produced by oxygen vacancies. The fall in the conductivity beyond an optimum duration of heating may be attributed to the saturation of oxygen vacancies. In addition, as the

concentration of the conduction electrons became higher, Fermi energy seemed to be shifted upward and conduction behaviour also changed.

4. Conclusions

It has been indicated that the CS route produced sinteractive, fine particle and large surface area MgIn_2O_4 powder. The synthesis temperature is 200°C lower than that of the literature value [9]. This is attributed to the high reactivity of the combustion derived powder because of the thermal shock created by the higher flame temperature which existed for a short duration. The powder density of the sintered MgIn_2O_4 sample is greater than 95% of theoretical value. The optical band gap of combustion derived MgIn_2O_4 powder is 4.3 eV, which is greater than that of ITO and hence makes it a very good transparent conducting oxide material. Highest conductivity is obtained when the pellet is heated in H_2 atmosphere at 200°C for 6 h and the value is $5.57 \times 10^0 \text{ S cm}^{-1}$. Combustion derived MgIn_2O_4 powder is found to be n-type semiconductor by hot probe method. These results clearly indicate that the CS is the best route for the preparation of high purity, homogeneous and fine particles of mixed semiconductor oxide materials at relatively low temperatures.

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