

Synthesis and characterization of Aln_2O_4 indates, $A = \text{Mg, Ca, Sr, Ba}$

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Transparent conducting oxides, due to their high transparency and conductivity of the order of 10^2 S cm^{-1} , are competing candidates for a variety of technologically important applications such as liquid crystal displays, computer monitors etc. Conventional materials include indium tin oxide (ITO), zinc oxide (ZnO) and tin oxide (SnO_2). Higher transparency and/or higher conductivity than those of the materials commercially available are the need of the day in the development of photoelectronic devices with higher functions. It has been reported that MgIn_2O_4 , a spinel oxide, has high electrical conductivity and is capable of transmitting more ultraviolet radiation than ITO [1]. MgIn_2O_4 crystallizes in cubic symmetry having space group $\text{Fd}\bar{3}\text{m}$ and lattice parameter $a = 0.8864 \text{ nm}$ ($Z = 8$) [2]. The structure of MgIn_2O_4 is basically constituted by the close packing of oxygen ions. Oxygen occupies the corners of the polyhedra. The structure consists of rutile chains running parallel to the (110) direction. The chains are connected to each other by the cations existing in the tetrahedral sites. Spinel has many unoccupied cation sites in the unit cell. There are 64 equivalent tetrahedral cation sites and 32 octahedral sites in the unit cell. Out of these seven-eighths of the tetrahedral sites and half of the octahedral sites are not occupied [3]. MgIn_2O_4 – $\text{Zn}_2\text{In}_2\text{O}_5$ films prepared using the magnetron sputtering technique were found to have high transparency with a resistivity of $3.9 \times 10^{-4} \Omega \text{ cm}$ [4].

Besides MgIn_2O_4 , the indates of calcium, strontium and barium are of interest from the viewpoint of practical applications. CaIn_2O_4 crystallizes in the orthorhombic symmetry system having space group $\text{Pca}2_1$ or Pbcm [5]. Reid has shown that CaIn_2O_4 has a CaFe_2O_4 type structure and is isomorphous with CaSc_2O_4 and with NaScTiO_4 [6]. SrIn_2O_4 also has orthorhombic symmetry with space group Pnam [7]. Lalla and Muller-Buschbaum have shown that BaIn_2O_4 crystallizes with monoclinic symmetry having space group $\text{P}2_1/\text{a}$, and it represents a new structure type with relationships to BaSc_2O_4 [8].

Systematic study of the oxide indate ceramics is expected to provide fundamental understanding of the crystal chemistry of these materials and consequently better device design prospects. Many researchers are now attempting to prepare these materials using special processing techniques such as the sol–gel method and combustion techniques, which will be useful either in the reduction of the synthesis temperature or better control over the

particle size, thereby achieving improved properties. Combustion synthesis (CS) was found to be successful in preparing many metastable phases and also conventional materials at low temperatures [9]. In conventional solid state reaction (SSR), the oxides of the starting materials are mixed together and fired at higher temperatures. However, atomic level mixing is not possible and also agglomeration may occur. In the CS route, the nitrates of the starting materials are in solution form, which facilitates ionic level mixing of the constituents and leads to the formation of mixed oxides at lower temperatures than by the solid state reaction. It is of interest to compare these two methods in the synthesis of mixed oxide powders and their influence on monophasic formation and crystallization of the powders. In this letter, the synthesis of various indates with general formula Aln_2O_4 ($A = \text{Mg, Ca, Sr, Ba}$) by SSR and CS is reported. Characterization carried out using X-ray diffraction (XRD) and diffuse reflectance spectra is also reported.

In the SSR route, the indates of magnesium, calcium, barium and strontium were prepared by taking stoichiometric quantities of the respective carbonates and indium oxide. The powders were mixed thoroughly in acetone. All samples were calcined at 900°C for 24 h in air using a muffle furnace. Intermediate grinding was carried out to obtain uniformity and better reactivity. Samples were made into pellets of diameter 12 mm by applying a pressure of 2 t cm^{-2} . The pellets were sintered at 950°C , 1000°C and 1200°C for 48 h followed by further heating at 1300°C for 60 h.

For the CS route, the indates were prepared by mixing stoichiometric quantities of their respective nitrates, indium nitrate and a calculated amount of urea as fuel in the ratio 1:2:7 [9]. Indium nitrate was prepared by dissolving the appropriate quantity in hot HNO_3 solution (1:1). The clear solutions, in 200 ml beakers, were placed in a furnace at 500°C . As the reaction was an exothermic one, the solution mixture underwent combustion for about 30 s. The resultant buffy mass, after grinding, was heated at 900°C for 36 h followed by further heating at 1050°C for 6 h.

The XRD patterns were recorded in a Jeol JDX-8030 X-ray diffractometer with $\text{CuK}\alpha$ radiation in the 2θ range 10 – 85° . The particle sizes of the powders were analysed using a Malvern Instruments Easy Particle Sizer (M3.0). Lattice parameters were computed from 2θ values using a least squares refinement program. KBr was used as the internal

standard for correcting the instrumental errors. The density of the pellets was estimated using the weight loss technique. The diffuse reflectance spectra were recorded using a Hitachi U-3400 spectrophotometer with alumina as standard in the wavelength region of 200–800 nm.

Although the various indates studied have the same general formula AlIn_2O_4 , they crystallize in different structures. This is mainly attributed to the variation in the cationic sizes since monophase formation occurs at lower temperature for the larger cationic size compounds. Compared with all other indates, MgIn_2O_4 has smaller cationic size and its synthesis temperature is higher. By SSR, monophase of magnesium indate, calcium indate, strontium indate and barium indate occurs at 1300, 1200, 1000 and 950 °C, respectively, but by CS, up to 1050 °C, phase formation does not occur in the case of magnesium indate and only 46.29% of phase formation occurs for calcium indate. Monophase formation of strontium indate and barium indate occurs at 700 °C and 1050 °C, respectively. Subsequent heat treatment only leads to an increase in the intensity of the peaks and better crystallinity of the samples. The relative phase formation is estimated from the relations [10]:

$$\text{AlIn}_2\text{O}_4(\%) = (I_a/I_a + I_b) \times 100$$

$$\text{In}_2\text{O}_3(\%) = (I_b/I_a + I_b) \times 100$$

where I_a is the maximum intensity of the corresponding AlIn_2O_4 peak and I_b is the maximum intensity of the In_2O_3 peak. The results are listed in Table I.

Powder X-ray patterns of magnesium indate, calcium indate, strontium indate and barium indate were indexed on the basis of cubic, orthorhombic, orthorhombic and monoclinic structures, respectively

TABLE I Percentages of various indate phases

Synthesis route	Composition	Temperature (°C)	Indate (%)
SSR	MgIn_2O_4	950	8.69
		1000	28.18
		1200	43.92
		1300	100.00
	CaIn_2O_4	900	39.22
		950	74.16
		1000	96.72
	SrIn_2O_4	900	45.46
		950	75.76
	BaIn_2O_4	1000	100.00
		900	42.07
		950	100.00
CS	CaIn_2O_4	900	42.63
		1050	46.29
		1100	53.72
	SrIn_2O_4	As prepared	20.00
		600	64.04
	BaIn_2O_4	700	100.00
		900	40.91
		1050	100.00

[2, 5, 7, 8]. Figs 1–7 give the XRD patterns of magnesium indate, calcium indate, strontium indate and barium indate, heat treated at different temperatures, both by SSR and CS.

The lattice parameters, density and optical band gap values are given in Tables II and Table III. The agreement of the lattice parameters with the literature is good. The density of the samples prepared by SSR was found to be more than 80% of the theoretical density, while that for the powders prepared by the CS route was more than 90%. The particle sizes of the samples are found to be in the range 7–28 μm .

The diffuse reflectance spectra of the samples prepared by both SSR and CS are shown in Figs 8 and 9. A decrease of reflectance was noted in the case of MgIn_2O_4 from 500 to 800 nm, caused by conduction electrons. The fundamental absorption edge of all indates appeared between 250 and 400 nm, which is a shorter wavelength than ITO [1]. This shows that the optical band gaps of all indates are larger than that of In_2O_3 . The optical transmittance of all indates was much higher than that of ITO in the blue region (400–500 nm), which is important for application in full coloured LCDs. In the case of calcium indate, two peaks were observed. These were attributed to the multiphasic

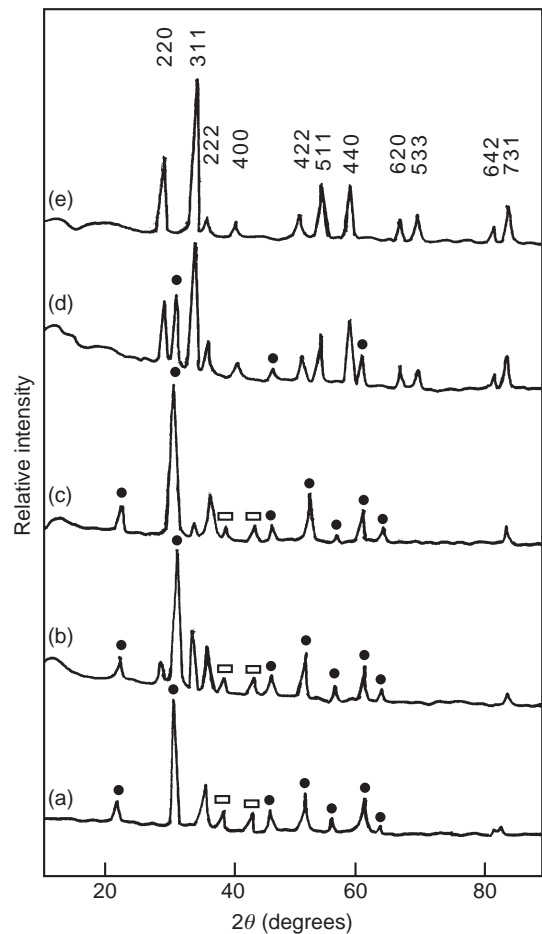


Figure 1 Powder XRD patterns of MgIn_2O_4 heated at different temperatures by SSR. (a) 900 °C, (b) 950 °C, (c) 1000 °C for 24 h, (d) 1200 °C for 48 h and (e) 1300 °C for 60 h. (□), MgO ; (●), In_2O_3 .

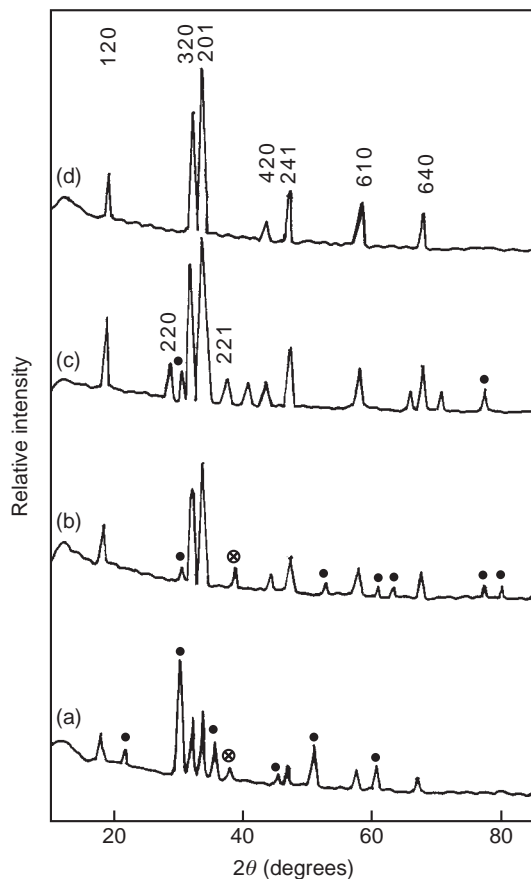


Figure 2 Powder XRD patterns of CaIn_2O_4 heated at different temperatures by SSR. (a) 900 °C, (b) 950 °C, (c) 1000 °C for 24 h and (d) 1200 °C for 48 h. (⊗), CaO; (●), In_2O_3 .

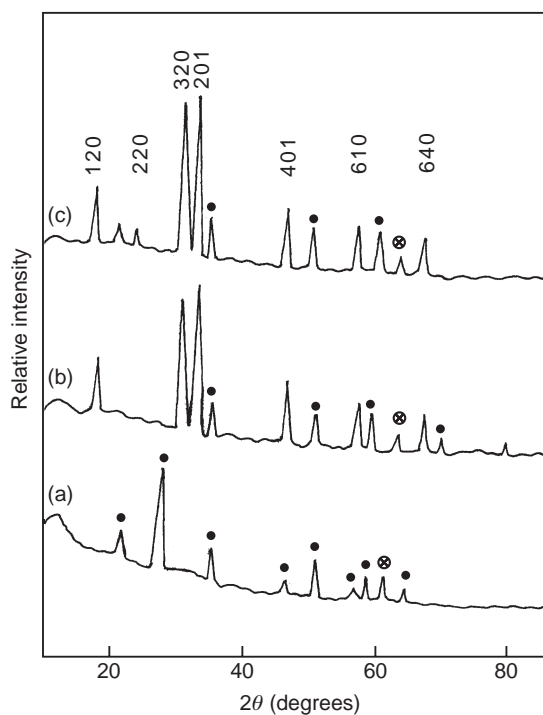


Figure 3 Powder XRD patterns of CaIn_2O_4 heated at different temperatures by CS. (a) As-prepared, (b) 900 °C for 36 h and (c) 1050 °C for 6 h. (⊗), CaO; (●), In_2O_3 .

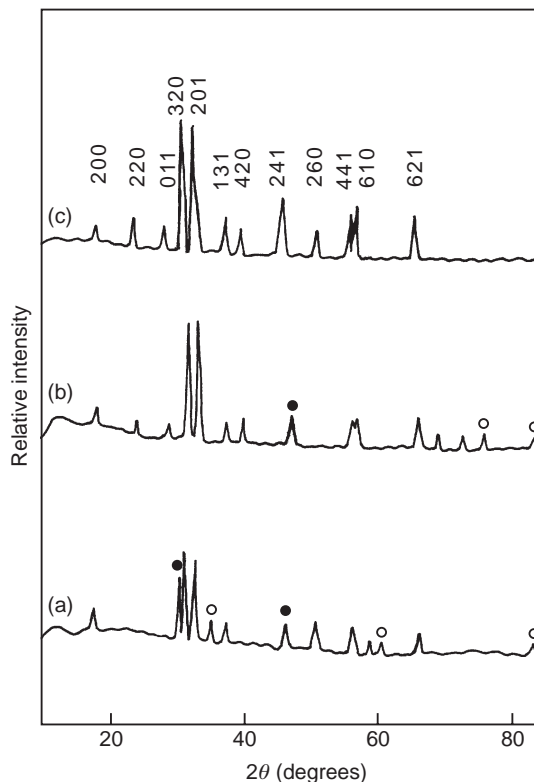


Figure 4 Powder XRD patterns of SrIn_2O_4 heated at different temperatures by SSR. (a) 900 °C, (b) 950 °C and (c) 1000 °C for 24 h. (○), SrO; (●), In_2O_3 .

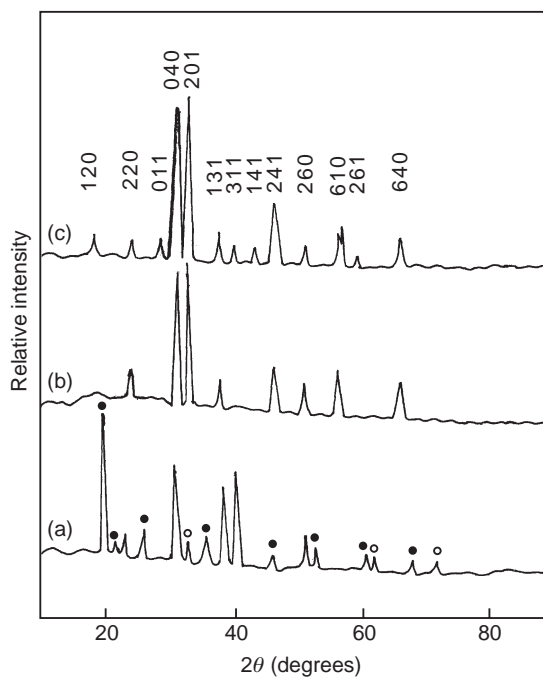


Figure 5 Powder XRD patterns of SrIn_2O_4 heated at different temperatures by CS. (a) As-prepared, (b) 900 °C for 36 h and (c) 1050 °C for 6 h. (○), SrO; (●), In_2O_3 .

nature of the samples observed in the XRD pattern. The absorption edge of the second peak just coincided with the absorption edge of standard In_2O_3 . The optical band gaps of magnesium indate,

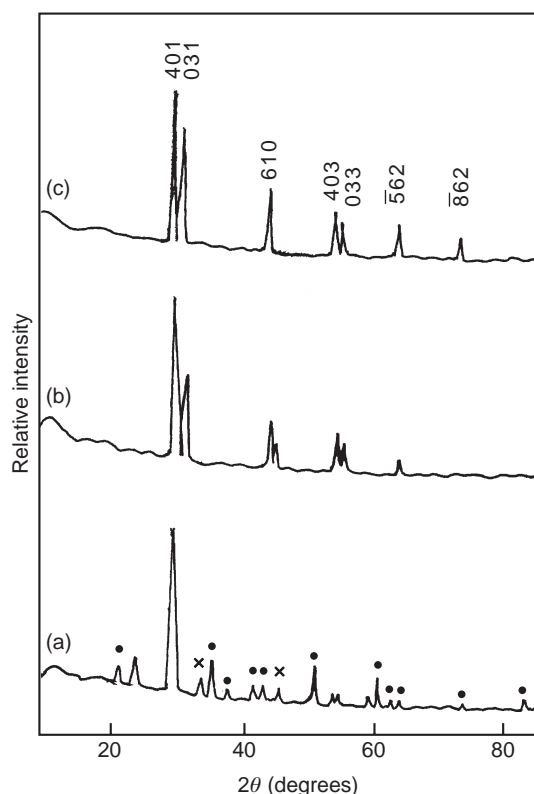


Figure 6 Powder XRD patterns of BaIn_2O_4 heated at different temperatures by SSR. (a) 900 °C, (b) 950 °C and (c) 1000 °C for 24 h. (×), BaO; (●), In_2O_3 .

calcium indiate, strontium indiate and barium indiate prepared by SSR were 3.1, 3.9, 3.6 and 3.2 eV; those of calcium indiate, strontium indiate and barium indiate prepared by CS were 4.0, 4.2 and 4.0 eV. The variation in band gaps prepared by the two techniques was due to the variation in the particle

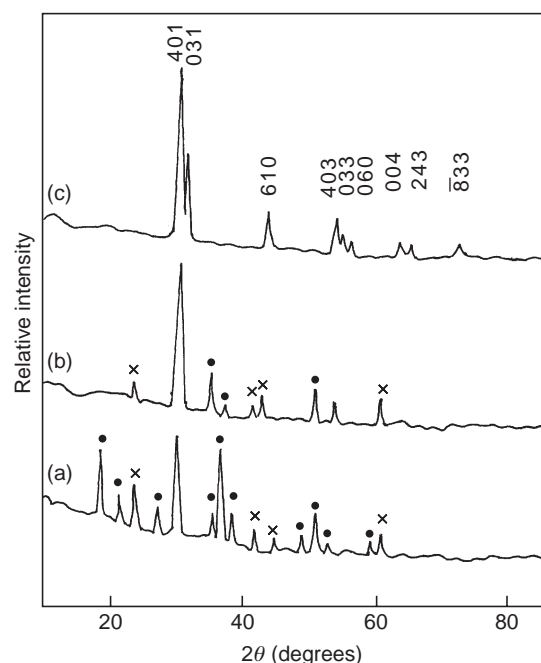


Figure 7 Powder XRD patterns of BaIn_2O_4 heated at different temperatures by CS. (a) As-prepared, (b) 900 °C for 36 h and (c) 1050 °C for 6 h. (×), BaO; (●), In_2O_3 .

size. The band gaps of the various indiates reported here were greater than 3 eV, and these indiates may be useful as transparent conducting oxide materials.

In conclusion, it was observed that the CS route produced monophasic strontium indiate powder at a lower temperature compared to that obtained by the SSR route. The synthesis temperature depends on the melting point of the parent oxides. In other words, the synthesis temperature is lower for lower melting point oxides and higher for higher melting point

TABLE II Lattice parameters, density and band gap of various indiate compositions prepared by SSR

Composition	System	Lattice parameter (nm)			Density			Band gap (eV)
		<i>a</i>	<i>b</i>	<i>c</i>	Theoretical (g cm^{-3})	Experimental (g cm^{-3})	TD (%)	
MgIn_2O_4	Cubic	0.886 (0.887)	–	–	6.06	5.15	85	3.1
CaIn_2O_4	Orthorhombic	0.970 (0.972)	1.130 (1.130)	0.321 (0.324)	6.15	5.23	85	3.9
SrIn_2O_4	Orthorhombic	0.983 (0.981)	1.150 (1.149)	0.327 (0.325)	6.86	5.99	87	3.6
BaIn_2O_4	Monoclinic	1.45 (1.34)	1.04 (1.00)	0.58 (0.61)	13.84	11.82	85	3.2

TABLE III Lattice parameters, density and band gap of various indiate compositions prepared by CS

Composition	System	Lattice parameter (nm)			Density			Band gap (eV)
		<i>a</i>	<i>b</i>	<i>c</i>	Theoretical (g cm^{-3})	Experimental (g cm^{-3})	TD (%)	
CaIn_2O_4	Orthorhombic	0.970 (0.973)	1.130 (1.133)	0.321 (0.323)	6.15	5.62	91	4.0
SrIn_2O_4	Orthorhombic	0.983 (0.980)	1.150 (1.150)	0.327 (0.328)	6.86	6.65	97	4.2
BaIn_2O_4	Monoclinic	1.45 (1.34)	1.04 (0.98)	0.58 (0.62)	13.84	12.56	91	4.0

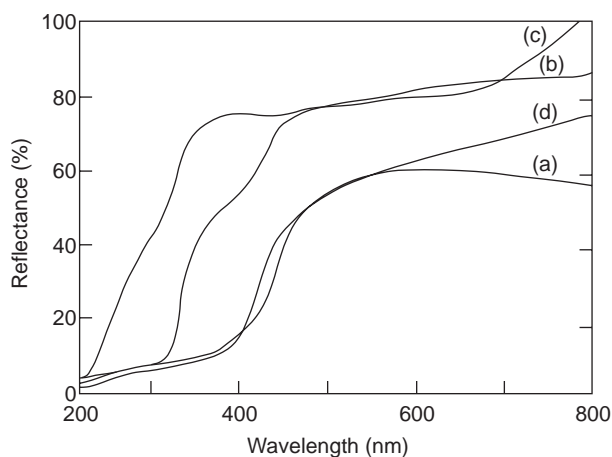


Figure 8 Diffuse reflectance spectra of (a) MgIn_2O_4 , (b) CaIn_2O_4 , (c) SrIn_2O_4 and (d) BaIn_2O_4 by SSR.

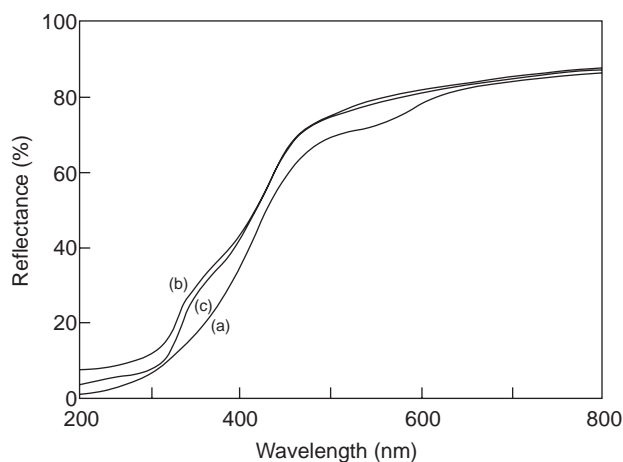


Figure 9 Diffuse reflectance spectra of (a) CaIn_2O_4 , (b) SrIn_2O_4 and (c) BaIn_2O_4 by CS and subsequent annealing at 900°C for 36 h.

oxides. Indate powders with general formula AlIn_2O_4 ($A = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$) prepared from a carbonate precursor have a low synthesis temperature compared to those prepared via the oxide precursor route.

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