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Increased conductivities of Cr doped $Al_{2-x}Cr_xO_3$ powders due to band gap narrowing

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ABSTRACT

A high Cr content in the synthesized $Al_{2-x}Cr_xO_3$ materials was achieved *via* a new synthesis route, the self propagating combustion method, for investigation of the effect of Cr substitution on the electrical, optical band gap and structural characteristics of the modified Al_2O_3 materials. X-ray diffraction (XRD) results showed that all the samples were pure and that Cr was successfully substituted in the crystal lattice. The cell parameters and volume are linearly dependent on the Cr content. AC impedance spectroscopy results show that conductivity of the Cr doped samples increases exponentially with Cr content. This is attributed to band gap narrowing of the $Al_{2-x}Cr_xO_3$ powders as obtained from UV–visible spectrophotometric studies.

1. Introduction

Corundum or α-Al_2O_3 is the most stable form of aluminium oxide. It is known that Al_2O_3 is highly insulating with a large band gap of 8.8 eV [1–3]. The electrical properties of materials can be changed by doping [4]. Not much work has been done on the electrical effect of substitutional doping of metal oxide insulators such as Al_2O_3. It is therefore interesting to study the effects of doping on the electrical characteristics of Al_2O_3.

Corundum is a very stable compound with a high melting point of 2054 °C [5]. Therefore, it will not be easy to synthesize pure and single phase Cr substituted samples, $Al_{2-x}Cr_xO_3$, unless a suitable synthesis method is used and the thermal annealing is done at the correct temperature. In this work, substitutional doping of Cr in Al_2O_3 is done *via* a self propagating combustion synthesis method. This synthesis method is found to be useful in obtaining pure and single phase metal oxides with complex stoichiometries [6–8]. The conductivities of the $Al_{2-x}Cr_xO_3$ have been found to increase by the order of one in the highest Cr content sample, $Al_{1.7}Cr_{0.3}O_3$. It is also found that as the Cr content increases, band gap values decrease.

2. Experimental

Al_2O_3 and $Al_{2-x}Cr_xO_3$ (x=0.1, 0.2, 0.3) materials were prepared using a self-propagating combustion method. Starting materials of aluminium nitrate nonahydrate and chromium nitrate nonahydrate (Merck) both of 99.9% purity, were dissolved in ultra pure deionised water (from TKA Labtower (EDI:15–10 MΩ cm)). They were slowly heated at 200 °C until combustion occurs and then calcined at 1300 °C for 48 h for Al_2O_3 sample and for 30 h for $Al_{2-x}Cr_xO_3$ samples. The samples were designated as A, R1, R2 and R3 for Al_2O_3, $Al_{1.9}Cr_{0.1}O_3$, $Al_{1.8}Cr_{0.2}O_3$ and $Al_{1.7}Cr_{0.3}O_3$, respectively. Chromium oxide (Cr_2O_3) (Merck 99.9% purity) was used for comparison and designated as sample C.

The samples were then studied by X-ray powder diffraction (XRPD) (Pan Analytical X′Pert Pro XRD System) for structural studies. The Rietveld refinement software used was the PANalytical X′pert Highscore Plus. The refinement was done using the hexagonal crystal structure setting of the ICSD 75479 and ICSD 64988 for the Al_2O_3 and $Al_{2-x}Cr_xO_3$ respectively. Conductivity studies were done *via* AC Impedance Spectroscopic technique using a WONATECH WEIS510 Multichannel Electrochemical Impedance Spectroscopy (EIS) System with a frequency range between

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1 Hz and 1 MHz. The band gap studies were measured using a UV–vis NIR spectrophotometer (Perkin-Elmer Lambda 950) using a reflection optical geometry.

3. Results and discussion

Cr substitution in Al_2O_3 is difficult and can only be done at high temperatures. So, far, only 4% substitutional doping of Cr has been achieved by Cava et al. [9] who employed a polymeric precursor method. Our combustion synthesis method has successfully yielded a higher Cr content of 6 to 26% in the $Al_{2-x}Cr_xO_3$ powders. This illustrates that the combustion method is a good synthesis method for producing doped $Al_{2-x}Cr_xO_3$ materials. Fig. 1 of the indexed XRD patterns of $Al_{2-x}Cr_xO_3$ shows that the materials are pure and single phase. Crystallographic parameters listed in Table 1 are obtained from Rietveld refinements of the XRD datasets (shown in Fig. 2(a)–(e)). It is observed that with increasing Cr content, there is a linear increase of the cell parameters, *a* and *c*, as well as volume, V, as shown in Fig. 3. The high R^2 values in the linear regression graphs of Fig. 3 show a remarkable accuracy of the site occupancy factor determination from the Rietveld refinements. The increase of the cell parameters is due to the larger ionic radius of Cr (ionic radius of $Al^{3+}=0.54$ Å and $Cr^{3+}=0.62$ Å for coordination number 6 [10]) compared to Al. The XRD results prove that Cr has been substituted for Al in the crystal lattice.

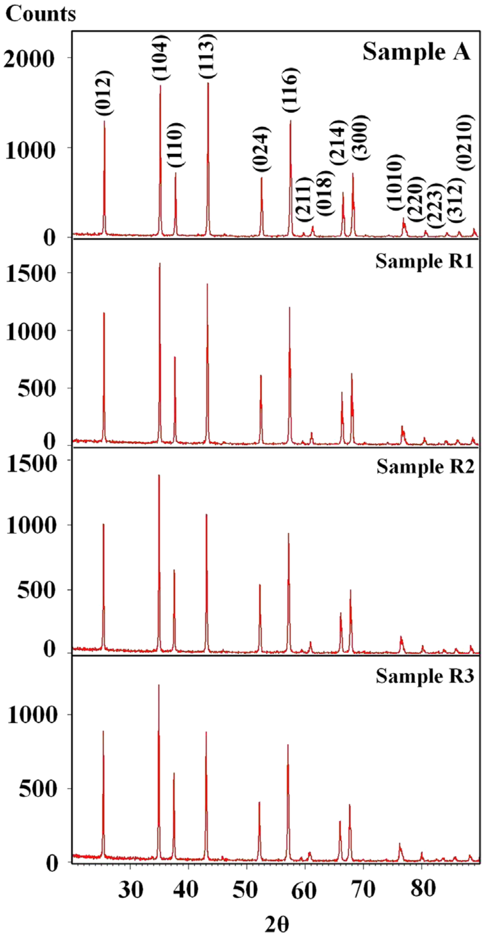

Fig. 1. XRD results of the indexed XRD patterns of sample A, R1, R2 and R3.

Fig. 4(a)–(e) shows Nyquist plots of the Al_2O_3, $Al_{2-x}Cr_xO_3$ and Cr_2O_3 materials. Only one semi-circle is observed implying a single time constant or Debye response for all the samples. The plots are analyzed using the ZMAN software with a circular fit. A Randles equivalent circuit is used in the fitting and the bulk impedance, R_b, are obtained in this way. The conductivity values of the samples are calculated using the well known Eq. (1) below.

$$\sigma=\frac{t}{AR_b} \tag{1}$$

where σ is the conductivity, t is the pellet thickness, A is the contact area of pellet with the electrode and R_b is the bulk resistance of the material [11].

Conductivity values are given in Table 1 and conductivity versus Cr content is shown in the graph of Fig. 4(f). The conductivity values seem to increase according to an exponential relation with Cr content. This is a new and novel finding.

To further understand the increase of conductivity with the dopant amount, band gap values are studied via the absorption edges of the UV–vis spectrum of the samples. The equation used is the well-known Tauc relation [12] given below,

$$(\alpha h\upsilon)=A(h\upsilon-E_g)^x \tag{2}$$

where α is the absorption coefficient of the material at a certain value of the wavelength λ, h is Planck′s constant, A is a proportionality constant, ν is the frequency of light, E_g is the band energy and $x=½$ (for direct transition mode materials) [13]. The electronic band transitions of all the materials are obtained from the Tauc plots shown in Fig. 5 and listed in Table 1. From the listed values, it is obvious that there is band gap narrowing of the samples as the Cr content increases. The decrease of the band gap explains why the conductivity of the Cr doped samples increases. Electrons from the highest occupied molecular orbital (HOMO) can jump into the lowest unoccupied molecular orbital (LUMO) in an easier manner when the band gap is narrower. Thus, conductivity rises. Considering the orbitals of the Al^{3+} ions, it can be seen that on bonding with oxygen, all the 2p electrons are paired and there is

Table 1
Crystallographic parameters of the samples from the Rietveld refinements of the XRD datasets (s.o.f.=site occupancy factor), conductivities and band gap energy of the samples.

Sample ID	Chemical formula	Cr (synthesized values) (%)	$a=b$ (Å)	c (Å)	V (Å^3)	R_w	χ^2	s.o.f of Cr	Conductivity σ (S cm^{-1})	Band gap energy ± 0.001 (eV)
A	Al_2O_3	0.00	4.7592	12.9924	254.8497	10.83	2.97	–	2.57×10^{-10}	8.8[a]
R1	$Al_{1.9}Cr_{0.1}O_3$	0.05	4.7711	13.0215	256.6982	9.61	2.27	0.031	4.36×10^{-10}	4.900
R2	$Al_{1.8}Cr_{0.2}O_3$	0.10	4.7826	13.0514	258.5362	9.06	2.30	0.070	5.98×10^{-10}	4.800
R3	$Al_{1.7}Cr_{0.3}O_3$	0.15	4.7936	13.0805	260.3075	9.00	2.23	0.130	6.83×10^{-9}	4.490
C	Cr_2O_3	1.00	4.9600	13.5969	289.6869	8.83	1.80	0.950	3.17×10^{-4}	3.230

[a] Values taken from R.H. French [1].

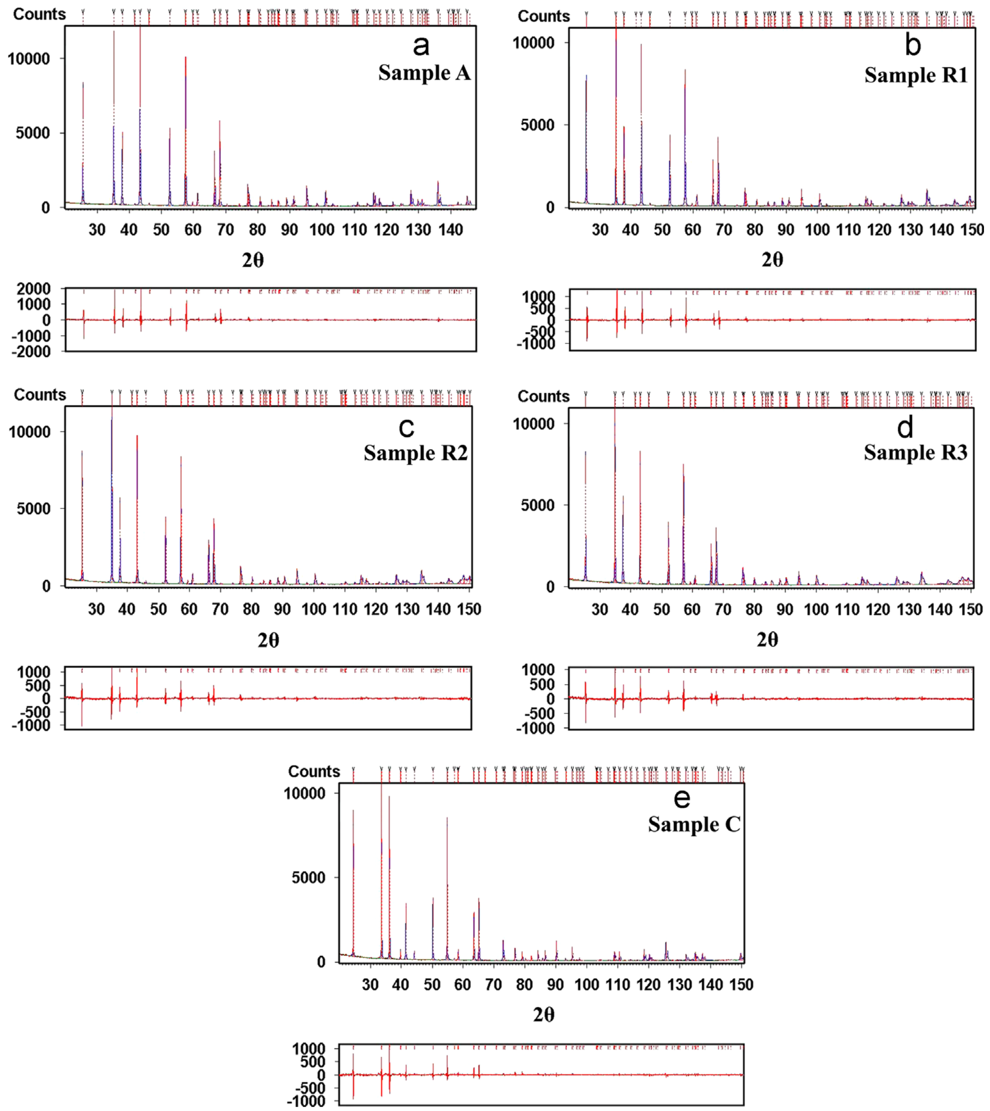

Fig. 2. Rietveld refinements of XRD patterns of (a) sample A, (b) sample R1, (c) sample R2 (d) sample R3 and (e) Sample C.

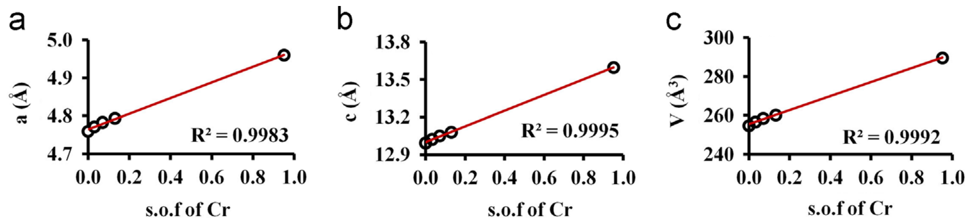

Fig. 3. Graphs showing the relationship of (a) a with s.o.f. of Cr (b) c with s.o.f. of Cr and (c) V with s.o.f. of Cr.

no crystal splitting occurring in the Al_2O_3. There are also no unpaired electrons in the electronic configuration of O^{2-}. The gap between the HOMO and LUMO in Al_2O_3 is large making it difficult for the electrons to jump into the conduction band. This explains why Al_2O_3 is an insulator. This also explains why Al_2O_3 has a very stable electronic configuration. The situation is different for the doped materials. The presence of the 3d transition metal ion, Cr^{3+}, results in three unpaired electrons and this causes crystal field splitting. The electrons in the d_{xy}, d_{xz} and d_{yz} orbitals can undergo transitions to the d_{z^2} and $d_{x^2-y^2}$ orbitals. Thus, Cr doping introduces more energy levels in the band structure of $Al_{2-x}Cr_xO_3$ materials making them more conducting.

4. Conclusions

Higher Cr content of the $Al_{2-x}Cr_xO_3$ materials have been successfully obtained using the combustion method. On doping with Cr, the energy levels of the substituted compounds are drastically modified by the presence of the transition metal ion, Cr^{3+}, increasing the

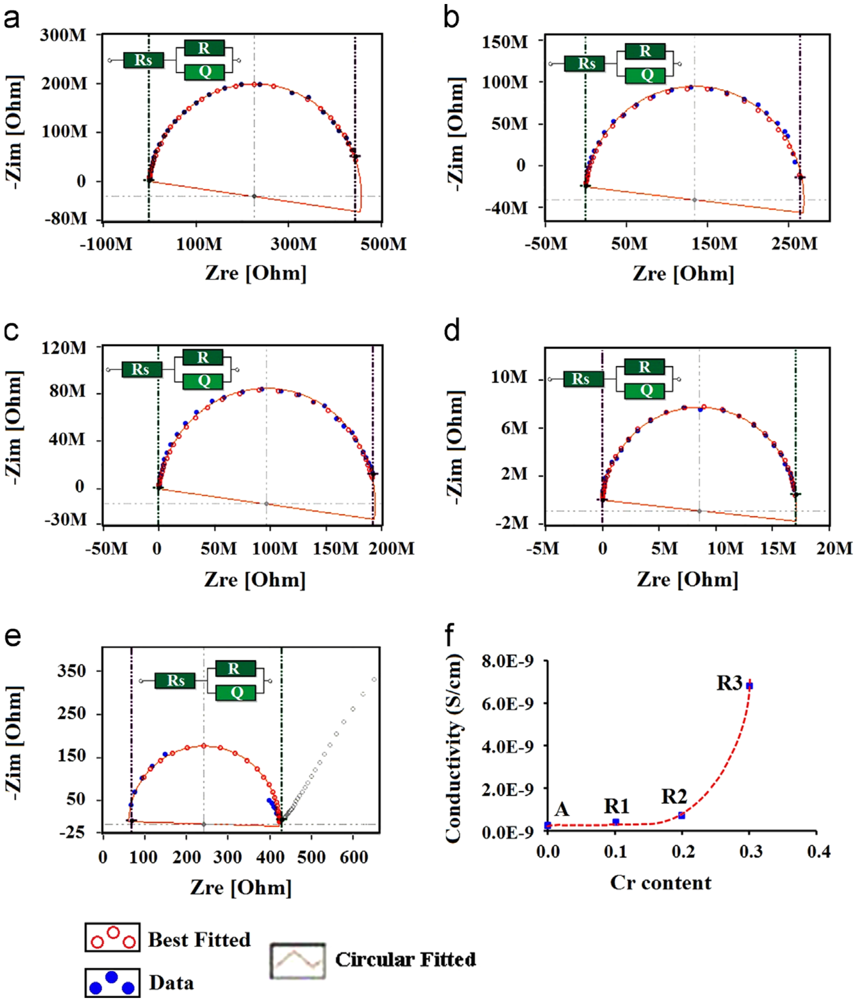

Fig. 4. Analyzed Nyquist plots using Zman software and fitted to the equivalent circuit shown for sample (a) Al_2O_3, (b) $Al_{1.9}Cr_{0.1}O_3$, (c) $Al_{1.8}Cr_{0.2}O_3$, (d) $Al_{1.7}Cr_{0.3}O_3$, (e) Cr_2O_3 and (f) graph showing the relationship between conductivity of the materials with Cr content.

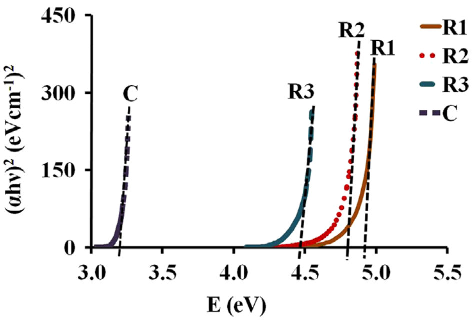

Fig. 5. Tauc plots for sample $Al_{1.9}Cr_{0.1}O_3$ (R1), $Al_{1.8}Cr_{0.2}O_3$ (R2), $Al_{1.7}Cr_{0.3}O_3$ (R3) and Cr_2O_3 (C).

conductivity of the materials. Band energy narrowing is the cause of the increased conductivity of the $Al_{2-x}Cr_xO_3$ materials.

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