Effect of doping of divalent and trivalent metal ions on the structural and electrical properties of magnesium aluminate

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Abstract

Nanosized magnesium aluminate materials doped by divalent cations (Ca^{2+}, Ba^{2+}, Sr^{2+}) and trivalent cations (Cr^{3+}, Mn^{3+}, Fe^{3+}) having nominal compositions $Mg_{1-x}M_xAl_2O_4$ and $MgAl_{2-x}M_xO_4$ ($x = 0.02$–0.1), respectively, were synesized by the sol–gel method. The samples were characterized by X-ray diffraction (XRD) and dc electrical resistivity measurements. The XRD data showed that all the samples were spinel single phase cubic closed packed crystalline materials having crystallite sizes between 6 and 35 nm. The lattice constant and X-ray density were found to be affected by the ionic radii of doped metal cations investigated here. Both the bulk density (d_b) and X-ray density (d_x) of doped materials increased whereas the porosity percentage (P) decreased with the increase in the contents of the substituents. The dc-electrical resistivity of all the samples was measured in temperature range 160–400 °C by a two-point probe method and was found to decrease with temperature as expected for semiconductors. It was observed that alkaline earth metal dopants increased the resistivity of $MgAl_2O_4$ more than that by transition metal dopants. Arhenius activation energy of hopping of electron for all the samples was also calculated.

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Keywords: Nanomaterials; Magnesium aluminate; dc-Electrical resistivity; Two-point probe method; X-ray density

1. Introduction

Nanophase materials (<100 nm) exhibit greatly altered physicochemical properties compared to their normal bulk counterparts [1–3]. Because of their theoretical and technological relevance, spinel magnesium aluminates and their related structures have been studied thoroughly. It is a mixed oxide whose physical properties range between those of magnesium oxide and aluminum oxide. Magnesium aluminate ($MgAl_2O_4$) spinel has received a great deal of attention as a technologically important material on account of its attractive properties such as high melting point (2135 °C), high mechanical strength at elevated temperatures, high chemical inertness and good thermal shock resistance [4–6]. Therefore, it has been extensively used for various purposes such as refractory material [7], catalyst or catalyst support in the field of environmental catalysis [8], active element in humidity sensors [9] and structural material in fusion reactors [10]. It has also been employed as an excellent transparent ceramic material for high-temperature arc-enclosing envelops and alkali-metal vapor discharge devices [11]. The physical properties of ceramic materials are influenced by the nature of grains, such as shape, size, orientation, grain boundaries, voids, inhomogeneities, etc. The electronic properties and electrical conductivity of mesoscopically small crystals change compared to their bulk counterparts owing to their small grain sizes. The change also depends on the large percentage of their atoms in grain boundary environments and the interactions between grains [12]. Studies concerning substitution of Ce^{3+}, Cr^{3+}, Mn^{3+} and Ti^{2+} at Al^{3+} site of $MgAl_2O_4$ spinel have been carried out by several workers [13–16]. The synthesis of Ca^{2+}, Ba^{2+}, Sr^{2+}, Cr^{3+}, Mn^{3+} and Fe^{3+} substituted $MgAl_2O_4$ nanoparticles in order to investigate the substitution effect on structural and electrical properties is the focus of the present study.

2. Experimental

The compounds used in the synthesis of samples were of analytical grade i.e. $Al(NO_3)_3 \cdot 9H_2O$ (Merck, 95.0%), $Mg(NO_3)_2 \cdot 6H_2O$ (Merck, 99.9%), ethylene glycol (Merck, 99.0%) and aqueous NH_3 (Reidal, 33.0%) and were therefore used as such. Samples were prepared by the sol–gel method [17].

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In the sol–gel method, aqueous solutions of magnesium nitrate and aluminum nitrate in a molar ratio (Mg/Al = 0.5) were mixed with aqueous solution of ethylene glycol in ratio 0.5 of mixed metal nitrate/glycol. Ammonia solution was added drop wise with constant stirring to maintain the pH value at about 5 and was monitored by a pH-meter (Horiba, HM-7E). The sample was evaporated with constant stirring on a hot plate with magnetic stirrer (Velp, model ARE) at 120 °C for 10 h till dryness. The powdered sample was then calcined in air using a temperature programmed tube furnace (Carbolite, CFT 12/100) at a heating rate of 5 °C/min up to 800 °C. The cation doped derivatives of $MgAl_2O_4$ were also prepared by adding the appropriate stoichiometric quantities of the dopants following the same procedure. The X-ray diffraction analysis was performed by an X-ray diffractometer (Jeol JDX-60PX) using Cu Kα radiation source, at 45 kV and 40 mA. Data were collected in the 2θ range from 10° to 90° with a step 0.04° and counting time of 1 s/step. Diffraction peaks were used to identify the structure of the samples by matching with the standard pattern of the magnesium aluminate spinel. The crystallite size was determined using the Scherrer formula [18] (Eq. (2)). The dc electrical resistivity was measured in a temperature range of 160–400 °C using a laboratory made equipment by a two-point probe method [19].

3. Results and discussions

XRD patterns of pure $MgAl_2O_4$, $Mg_{1-x}M_xAl_2O_4$ (M = Ca^{2+}, Ba^{2+}, Sr^{2+}) and $MgAl_{2-x}M_xO_4$, (M = Cr^{3+}, Mn^{3+}, Fe^{3+}) and x = (0.02–0.6) are shown in Figs. 1–6. Fig. 1(a) shows the peaks corresponding to (1 1 1), (2 2 0), (3 1 1), (4 0 0), (5 1 1)

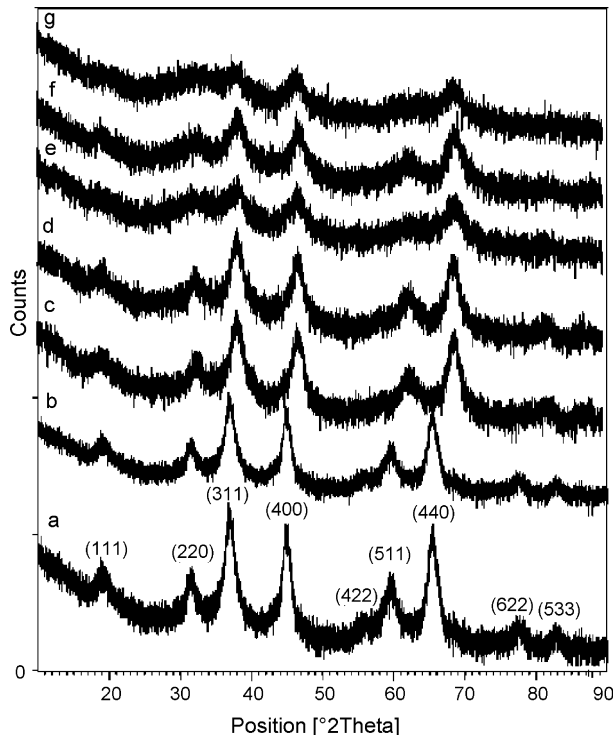and (4 4 0) reflection of standard $MgAl_2O_4$ pattern (JCPDS Card No. 21–1152). The temperature for obtaining the well crystallized and highly pure $MgAl_2O_4$ spinel phase has already been optimized [20]. It is evident from Figs. 1–6 that a single spinel phase has been formed in all the samples. The value of
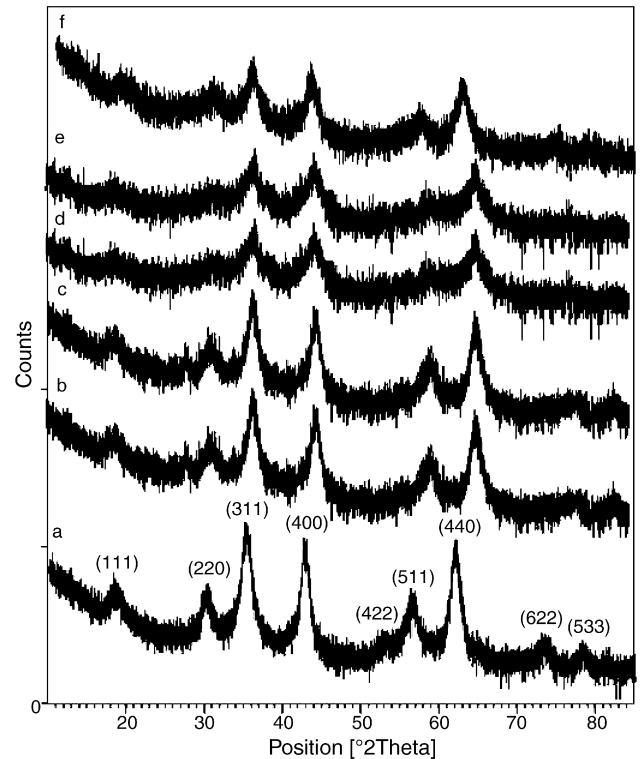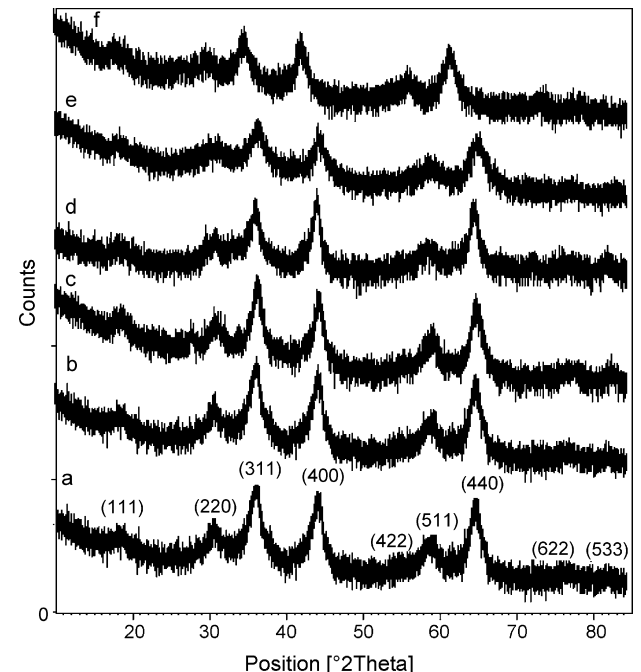

Fig. 2. Comparison of XRD patterns of $Mg_{1-x}Ba_xAl_2O_4$ where: (a) x = 0.00; (b) x = 0.02; (c) x = 0.04; (d) x = 0.06; (e) x = 0.08; (f) x = 0.1.

Fig. 1. Comparison of XRD patterns of $Mg_{1-x}Ca_xAl_2O_4$ where: (a) x = 0.0; (b) x = 0.1; (c) x = 0.2; (d) x = 0.3; (e) x = 0.4; (f) x = 0.5; (g) x = 0.6.

Fig. 3. Comparison of XRD patterns of $Mg_{1-x}Sr_xAl_2O_4$ where: (a) x = 0.00; (b) x = 0.02; (c) x = 0.04; (d) x = 0.06; (e) x = 0.08; (f) x = 0.1.