

Short communication

# Combustion synthesis of $\text{Ca}_{1-x}\text{Cu}_x\text{Al}_2\text{O}_4$ ( $x = 0.0, 0.4$ and $0.8$ ) copper doped calcium aluminate

K.S. Madhana Kumar<sup>a</sup>, L. John Berchmans<sup>b,\*</sup>

<sup>a</sup>Department of Materials Science, Madurai Kamaraj University, Palkalai Nagar, Madurai 625 021, India

<sup>b</sup>Electroprometallurgy Division, Central Electrochemical Research Institute, Karaikudi 630 006, India

Received 18 January 2008; received in revised form 19 February 2008; accepted 9 April 2008

Available online 16 July 2008

## Abstract

We report the effect of  $\text{Cu}^{2+}$  ion on  $\text{CaAl}_2\text{O}_4$  with different molar concentrations of 0.0, 0.4 and 0.8 M prepared by simple combustion method. The materials have been characterized by X-ray diffraction (XRD), Fourier transform infrared spectra (FT-IR) and scanning electron microscopy (SEM). DC electrical conductivity has also been measured to study the electrical behavior of the materials. The XRD patterns confirm the formation of single-phase  $\text{CaAl}_2\text{O}_4$  along with some impurity phases like  $\text{CaAl}_4\text{O}_7$ ,  $\text{CaAl}_{12}\text{O}_{19}$  and  $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ . The FT-IR spectra show the stretching and bending vibrations of the synthesized compounds. DC electrical conductivity of the  $\text{Ca}_{1-x}\text{Cu}_x\text{Al}_2\text{O}_4$  is found to vary from  $26.46 \times 10^{-4}$  to  $515.68 \times 10^{-4} \text{ S cm}^{-1}$  for  $x = 0.0$  to  $x = 0.8$  at the measuring temperature of  $1000^\circ\text{C}$ . SEM images show the morphological features of the compounds.

© 2008 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

**Keywords:** Calcium aluminate; Electrical properties; X-ray diffraction; FT-IR; SEM

## 1. Introduction

Monocalcium aluminate,  $\text{CaAl}_2\text{O}_4$ , finds potential applications as refractory castables, high strength polymer modified cement based materials, optical and structural ceramics [1]. Recently, a number of investigations are striking about the applications of calcium aluminate as luminescent host materials for  $\text{Eu}^{2+}$  and  $\text{Nd}^{3+}$  as emission centre and auxiliary activator [2–4]. It is reported that the monocalcium aluminate prepared through solid-state reaction requires intermediate grinding and prolonged calcination at elevated temperatures. It shows poor sinterability with some impurity phases [1,5]. Wet chemical methods are preferred for ceramic materials preparation since they show high sinterability, high surface area with required stoichiometry. Wet chemical methods have been tried to synthesis  $\text{CaAl}_2\text{O}_4$  using combustion synthesis [4,6] co-precipitation [7], sol–gel [8] and Pechini process [9].

The primary aluminium is produced by Hall–Heroult process by the electro decomposition of alumina in cryolite melt at  $960^\circ\text{C}$ , using consumable carbon anodes. During

electrolysis, aluminium metal is deposited at the cathode with the evolution of  $\text{CO}_2$  and  $\text{CO}$  at the anode. Recently, ferrites and aluminates have been tried as alternate anode materials for aluminium production [10]. These anodes produce environmentally friendly  $\text{O}_2$  gas during electrolysis instead of greenhouse gases. In this context, we have already reported  $\text{Ce}^{4+}$  substituted  $\text{NiAl}_2\text{O}_4$  [11],  $\text{Mg}^{2+}$  substituted  $\text{NiFe}_2\text{O}_4$  [10] and  $\text{Sn}^{4+}$  substituted  $\text{NiFe}_2\text{O}_4$  [12]. In continuation of our studies, we have prepared copper substituted  $\text{CaAl}_2\text{O}_4$  using combustion method. The structural properties of the materials are characterized using X-ray diffraction (XRD) and Fourier transform infrared spectra (FT-IR) technique. The electrical properties have been studied by four-probe method from room temperature to  $1000^\circ\text{C}$ . The morphological features of the crystals have been examined using scanning electron microscopy (SEM). The results obtained from the above studies are discussed in this letter.

## 2. Experimental procedure

Copper substituted calcium aluminates were prepared from stoichiometric quantities of calcium nitrate tetrahydrate ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ), copper nitrate trihydrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ )

\* Corresponding author. Tel.: +91 4565 227550; fax: +91 4565 227713.

E-mail address: [ljburchmans@yahoo.com](mailto:ljburchmans@yahoo.com) (L. John Berchmans).

3H<sub>2</sub>O) and aluminium nitrate nonahydrate (Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) as cation sources. Citric acid monohydrate (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>·H<sub>2</sub>O) was used as the fuel. The metal nitrate salts and citric acid were dissolved in triple distilled water and heated in a quartz container around 300 °C. Initially the solution boiled and underwent dehydration followed by decomposition with the evolution of copious amounts of heat and gases. The mixture was then frothed and swelled forming foam, which then ruptured with a flame. The foamy powders were then heated in an electrical furnace at 1000 °C for 5 h. After sintering the powders showed colors ranging from white to pale brown depending upon the concentration of copper.

The powder X-ray patterns of the products were obtained using JEOL 8030 X-ray diffractometer with Cu K $\alpha$  irradiation ( $\lambda = 1.541 \text{ \AA}$ ). FT-IR spectra of the samples were recorded in a FT-IR, PerkinElmer UK Paragon-500 spectrometer. DC electrical conductivity was measured as a function of temperature using a four-probe setup from room temperature to 1000 °C [13]. The morphological features of the powders were examined using a scanning electron microscope JEOL (JSM-3.5 CF) Japan-make.

### 3. Results and discussion

The powder diffraction patterns of the sintered CaAl<sub>2</sub>O<sub>4</sub> and substituted compounds Ca<sub>1-x</sub>Cu<sub>x</sub>Al<sub>2</sub>O<sub>4</sub> are shown in Fig. 1.

The XRD patterns show well-defined peaks, which indicate the crystallinity and phase formation of the synthesized compounds. In addition to CaAl<sub>2</sub>O<sub>4</sub>, some impurity phases like CaAl<sub>4</sub>O<sub>7</sub>, CaAl<sub>12</sub>O<sub>19</sub> and Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> are also seen as secondary phases. This behavior is attributed to the fact that citric acid is a weak acid with low calorific value [9,14]. So, the heat needed to form the single-phase monocalcium aluminate is very low at the end of combustion process. Even after sintering at 1000 °C, some secondary phases are seen due to the slow conversion of these phases to form single-phase CaAl<sub>2</sub>O<sub>4</sub> [3]. The lattice constant values, X-ray density and crystallite size of the synthesized compounds are calculated and presented in Table 1.

The lattice constant values are found to decrease with increase in Cu<sup>2+</sup> ions. This may be due to the difference between the ionic radii of calcium (0.099 nm) and copper ions (0.072 nm). The calculated lattice constant values are in good agreement with the

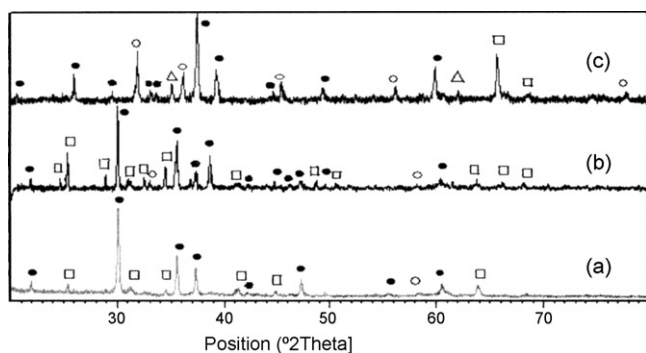


Fig. 1. XRD pattern of Ca<sub>1-x</sub>Cu<sub>x</sub>Al<sub>2</sub>O<sub>4</sub>. (a)  $x = 0$ , (b)  $x = 0.4$  and (c)  $x = 0.8$ . (●) CaAl<sub>2</sub>O<sub>4</sub>, (□) CaAl<sub>4</sub>O<sub>7</sub>, (○) CaAl<sub>12</sub>O<sub>19</sub>, (△) Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>.

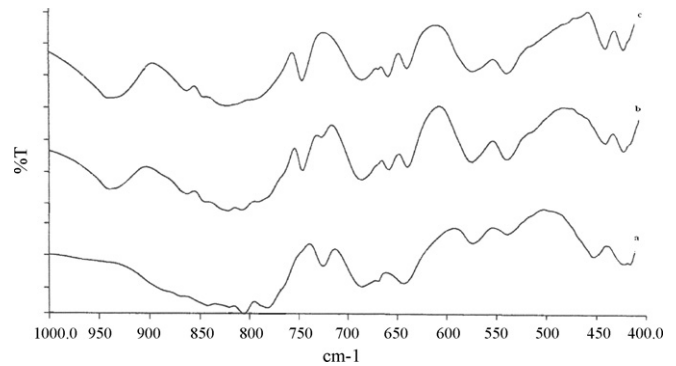


Fig. 2. FT-IR spectra of Ca<sub>1-x</sub>Cu<sub>x</sub>Al<sub>2</sub>O<sub>4</sub>. (a)  $x = 0$ , (b)  $x = 0.4$  and (c)  $x = 0.8$ .

reported values (JCPDS file No. 70-0134). X-ray density is calculated using the formula  $D_{hkl} = 8 M / Na^3$ . Due to higher density of copper than calcium, the X-ray density of the products increases with substitution. The crystallite size has been calculated using Debye–Scherrer formula  $0.9\lambda / \beta \cos \theta$ . The values are found to decrease from 65.26 to 29.71 nm as the concentration of Cu<sup>2+</sup> ion increases from 0.0 to 0.8 M.

The FT-IR spectra of the samples are shown in Fig. 2.

The absorption bands at 685, 459 and 422 cm<sup>-1</sup> are attributed to the stretching vibration of Ca–O bond [15]. The band at 639 cm<sup>-1</sup> is due to spinel phase [16]. The bands at 575 and 538 cm<sup>-1</sup> are indicating the stretching vibration of Al–O for octahedrally coordinated aluminium ions [11,17]. The high frequency band is  $\nu_1$  shifts in the range 728–749 cm<sup>-1</sup> due to the preference of Cu<sup>2+</sup> ion towards octahedral sites [18]. A new band appears at 942 cm<sup>-1</sup> in the case of substituted compounds is found to be broaden with the increase in concentration of Cu<sup>2+</sup> ions. In addition to the predominant bands, some weak bands are appeared in all the spectra, which represent the presence of secondary phases.

The temperature dependence behavior of the DC electrical conductivity of Ca<sub>1-x</sub>Cu<sub>x</sub>Al<sub>2</sub>O<sub>4</sub> is shown in Fig. 3.

It can be seen that the conductivity increases with increase in temperature. It is noticed that parent CaAl<sub>2</sub>O<sub>4</sub> does not show any appreciable change in conductivity with respect to temperature. It shows a conductivity value of  $26.46 \times 10^{-4} \text{ S cm}^{-1}$  at 1000 °C. A highest value of  $515.68 \times 10^{-4} \text{ S cm}^{-1}$  is observed for the compound with 0.8 M of copper addition. The increase in conductivity with temperature is due to the mobility of the charge

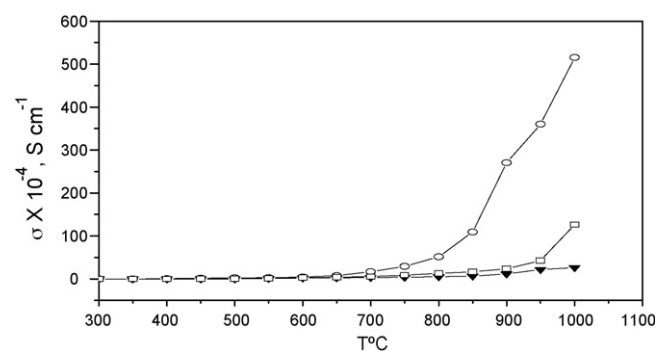


Fig. 3. Plot of DC electrical conductivity vs. temperature of Ca<sub>1-x</sub>Cu<sub>x</sub>Al<sub>2</sub>O<sub>4</sub>. (▼)  $x = 0$ , (□)  $x = 0.4$  and (○)  $x = 0.8$ .

Table 1  
XRD data of the samples prepared by combustion synthesis

Compound	Lattice constants			XRD density (g/cm <sup>3</sup> )	Crystallite size (nm)
	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)		
CaAl <sub>2</sub> O <sub>4</sub>	8.706	8.117	15.164	1.959	65.26
CaAl <sub>2</sub> O <sub>4</sub> (Cu = 0.4)	8.655	8.085	15.119	2.102	40.90
CaAl <sub>2</sub> O <sub>4</sub> (Cu = 0.8)	8.609	8.046	14.895	2.277	29.71

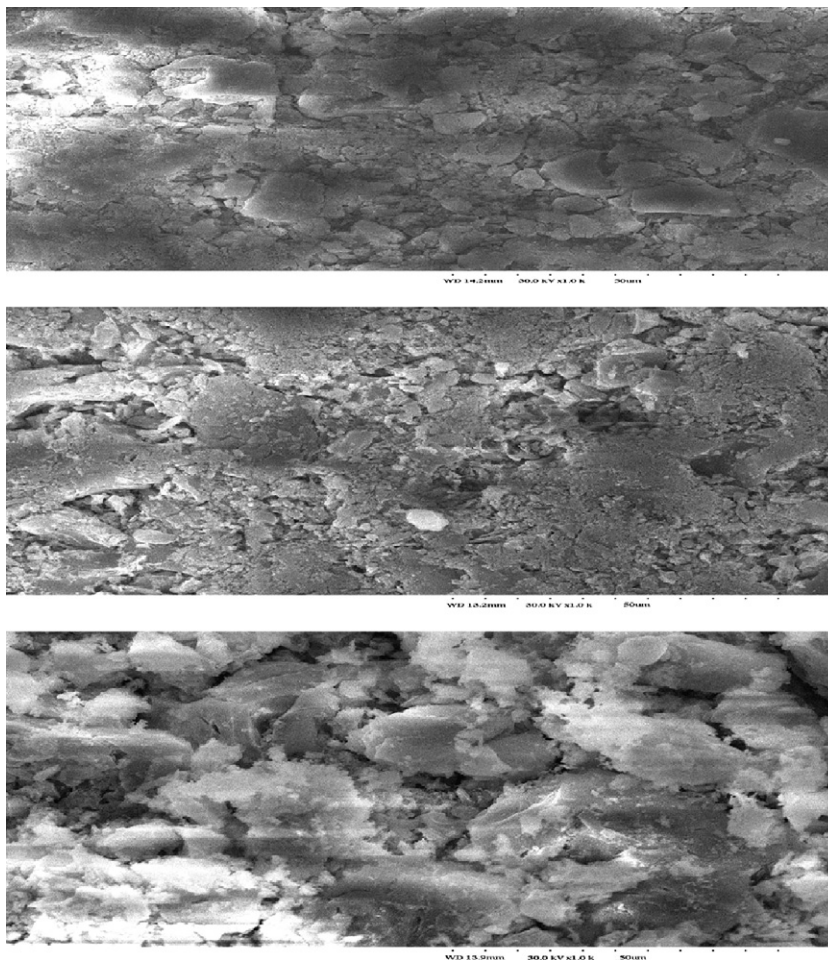
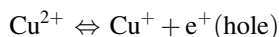


Fig. 4. SEM photos Ca<sub>1-x</sub>Cu<sub>x</sub>Al<sub>2</sub>O<sub>4</sub>, (a) *x* = 0, (b) *x* = 0.4 and (c) *x* = 0.8.

carriers as well as the migration of metallic Cu<sup>+</sup> ions [19]. The Cu<sup>+</sup> ions are made available by the reduction of Cu<sup>2+</sup> ions, which in turn makes excess holes according to the following mechanism [20]:



The conductivity of the compound Ca<sub>0.2</sub>Cu<sub>0.8</sub>Al<sub>2</sub>O<sub>4</sub> increases steadily up to 800 °C, after which a surge is observed due to large hopping of polarons. Generally, aluminates are poor conductors than ferrite materials, hence the conductivity of these ceramics are lying in the range of insulator–semiconductor.

The SEM micrographs of Ca<sub>1-x</sub>Cu<sub>x</sub>Al<sub>2</sub>O<sub>4</sub> (*x* = 0.0, 0.4 and 0.8) after sintering at 1000 °C are shown in Fig. 4

The micrographs are selected to be the representative of the size and texture of the grains. Fig. 4a and b consists of polygonal-shaped grains with small incrustations on the surface. The presence of these incrustations is probably due to the influence of secondary phases. As the substitution of Cu<sup>2+</sup> ion increases, the morphology has been modified and the grains are larger in size.

#### 4. Conclusions

The combustion synthesis is found to be a simple method for the preparation of aluminates. XRD patterns show the phase formation of CaAl<sub>2</sub>O<sub>4</sub> with some impure phases. FT-IR spectra exhibit the stretching and bending vibration of spinel aluminates. DC electrical conductivity studies reveal that the

synthesized compounds exhibit semi-conducting behavior at high temperatures. The maximum conductivity of  $515.68 \times 10^{-4} \text{ S cm}^{-1}$  is observed for the compound with the substitution of  $\text{Cu}^{2+}$  at 0.8.

## Acknowledgements

The authors are very much thankful to the Director, CECRI and all the staff members of Electroprometallurgy Division for their help to do this work.

## References

- [1] B.M. Mohamed, J.H. Sharp, Kinetics and mechanism of formation of monocalcium aluminate,  $\text{CaAl}_2\text{O}_4$ , *J. Mater. Chem.* 7 (1997) 1595–1599.
- [2] W. Jia, H. Yuan, H. Lu, Liu., W.M. Yen, Crystal growth and characterization of  $\text{Eu}^{2+}$ ,  $\text{Dy}^{3+}$ : $\text{SrAl}_2\text{O}_4$  and  $\text{Eu}^{2+}$ ,  $\text{Nd}^{3+}$ : $\text{CaAl}_2\text{O}_4$  by the LHPG method, *J. Cryst. Growth* 200 (1999) 179–184.
- [3] S. Tanaka, I. Ozaki, T. Kunimoto, K. Ohmi, H. Kobayashi, Blue emitting  $\text{CaAl}_2\text{O}_4$ : $\text{Eu}^{2+}$ , phosphorus for PDF application, *J. Lumin.* 87–89 (2000) 1250–1253.
- [4] J. Stanislava, S. Linda, R. Guillaume, F. Yaroslav, B. Damien, B. Philippe, Preparation and structural investigations of sol–gel derived  $\text{Eu}^{3+}$ -doped  $\text{CaAl}_2\text{O}_4$ , *J. Phys. Chem. Solids* 68s (2007) 1147–1151.
- [5] C. Zhao, D. Chen, Synthesis of  $\text{CaAl}_2\text{O}_4$ :Eu, Nd long persistent phosphor by combustion processes and its optical properties, *Mater. Lett.* 61 (2007) 3673–3675.
- [6] D.A. Fumo, M.R. Morelli, A.M. Segadaes, Combustion synthesis of calcium aluminates, *Mater. Res. Bull.* 31 (1996) 1243–1255.
- [7] Y.H. Lin, Z.T. Zhang, F. Zhang, Z.L. Tang, Q.M. Chen, Preparation of the ultrafine  $\text{SrAl}_2\text{O}_4$ :Eu, Dy needle-like phosphor and its optical properties, *Mater. Chem. Phys.* 65 (2000) 103–106.
- [8] T. Aitasalo, J. Holsa, H. Jungner, M. Lastusaari, J. Niittykoski, Sol–gel processed  $\text{Eu}^{2+}$ -doped alkaline earth aluminates, *J. Alloys Compd.* 341 (2002) 76–78.
- [9] A. Gaki, Th. Perraki, G. Kakali, Wet chemical synthesis of monocalcium aluminate, *J. Eur. Ceram. Soc.* 27 (2007) 1785–1789.
- [10] L. John Berchmans, K. Kalai Selvan, C.O. Augustin, Evaluation of  $\text{Mg}^{2+}$ -substituted  $\text{NiFe}_2\text{O}_4$  as a green anode material, *Mater. Lett.* 58 (2004) 1928–1933.
- [11] C.O. Augustin, K. Hema, R. Kalai Selvan, L. John Berchmans, R. Saraswathy, Effect of  $\text{Ce}^{4+}$  substitution on the structural, electrical and dielectric properties of  $\text{NiAl}_2\text{O}_4$  spinel, *Phys. Stat. Sol. A* 202 (2005) 1017–1024.
- [12] S. Balaji, R. Kalai Selvan, L. John Berchmans, S. Angappan, K. Subramanian, C.O. Augustin, Combustion synthesis and characterization of  $\text{Sn}^{4+}$  substituted nanocrystalline  $\text{NiFe}_2\text{O}_4$ , *Mater. Sci. Eng. B* 119 (2005) 119–124.
- [13] R. Kalaiselvan, C.O. Augustin, L. John Berchmans, R. Saraswathy, Combustion synthesis of  $\text{CuFe}_2\text{O}_4$ , *Mater. Res. Bull.* 38 (2003) 41–54.
- [14] P.N.M. Dos Anjos, E.C. Pereira, Y.G. Gobato, Study of the structure and optical properties of rare-earth-doped aluminate particles prepared by an amorphous citrate sol–gel process, *J. Alloys Compd.* 391 (2005) 277–283.
- [15] L. Shuzhi, Z. Bangwel, S. Xiaolin, O. Yifang Haowen, X. Zhongyu, The structure and infrared spectra of nanostructured  $\text{MgO}$ – $\text{Al}_2\text{O}_3$  solid solution powders prepared by the chemical method, *J. Mater. Technol.* 89–90 (1999) 405–409.
- [16] S. Janakova, L. Salavcova, G. Renaudin, Y. Filinchuk, D. Boyer, P. Boutinaud, Preparation and structural investigations of sol–gel derived  $\text{Eu}^{3+}$ -doped  $\text{CaAl}_2\text{O}_4$ , *J. Phys. Chem. Solids* 68 (2007) 1147–1151.
- [17] P. Jeevanandam, Yu. Kotypin, A. Gedanken, Preparation of nanosized nickel aluminate spinel by a sonochemical method, *Mater. Sci. Eng. B* 90 (2002) 125–132.
- [18] C.O. Arean, J.S. Diez Vinuela, J.M. Rubio Gonzalez, A. Mata Arjona, Crystal chemistry of  $\text{Cu}_x\text{Zn}_{1-x}\text{Al}_2\text{O}_4$  spinels, *Mater. Chem.* 6 (1981) 165–173.
- [19] L. John Berchmans, R. Kalai Selvan, P.N. Selva Kumar, C.O. Augustin, Structural and electrical properties of  $\text{Ni}_{1-x}\text{Mg}_x\text{Fe}_2\text{O}_4$  synthesized by citrate gel process, *J. Magn. Magn. Mater.* 279 (2004) 103–110.
- [20] R. Kalai Selvan, C.O. Augustin, L. John Berchmans, R. Saraswathy, Combustion synthesis of  $\text{CuFe}_2\text{O}_4$ , *Mater. Res. Bull.* 38 (2003) 41–54.