

Reduced Activation Energy of Iron and Copper Ion Doped Mullite which Can Be Used as a Substrate in Electronic Industry

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ABSTRACT

The crystallized mullite composite has been synthesized via sol-gel technique in the presence of transition metal ions such as iron and copper. The electrical resistivity and activation energy of the composites have been measured and their variation with concentration of the metal ion has been investigated. The resistivity of doped mullite decreases rapidly in the shorter temperature range and sharply in the higher temperature range. The decreasing resistivity is due to the 3d orbital electrons and the concentration of metal ions present. X-ray analysis confirms the presence of metal ions in mullite, which entered in the octahedral site. The Fe²⁺ and Cu²⁺ ions will substitute Al³⁺ ion in the octahedral site of mullite structure and most probably will be responsible for reducing the resistivity as well as the activation energy. Transition metal ion doped mullite-based ceramic can be considered as promising material as a substrate in the electronic industry, because of its reasonable atom density, its low activation characteristics, low thermal expansion coefficient and high mechanical strength. The present material we have developed has an activation energy of resistivity/band gap energy, Eg, 1.11 eV at 0.04 M concentration for Cu²⁺ ion.

Keywords: Nanostructures; Sol-Gel Growth; X-Ray Diffraction; Scanning Electron Microscopy (SEM); Electrical Conductivity

1. Introduction

Mullite is a material with an important role in the technology of classical and advanced ceramics due to high mechanical strength, low dielectric constant, high creep resistance and low thermal expansion coefficient [1-8]. Mullite based ceramic composites have been continually gaining importance in the insulator and semiconductor industry. Mullite formation starts from 1000°C due to solid-state reaction between Al₂O₃ and SiO₂ particles [9-15].

A wide variety of transition metals enter the mullite structure, Schneider *et al.* [2-4] has performed a systematic study in order to determine the solubility limit of various transition metal ions, as well as, the location of the corresponding cations in the structure [2-4,7]. The incorporation of transition metal ions strongly depends on their ionic radii and oxidation states, as well as syn-

thesis procedure. Trivalent cations with ionic radii close to Al³⁺ can readily be incorporated in mullite structure.

Mullite composites in the presence of various doping agents modifying the mechanical and chemical properties have been reported by many authors. However, literature concerning the activation energy (*Eg*) of metal ions doped mullite composites is relatively few [16-22].

This paper deals with the synthesis of mullite composites doped with varying concentrations of Fe²⁺ and Cu²⁺ ions and determines the effect of the same on activation energy of the composites. The divalent cations (M) with larger ionic radii rather react with Al₂O₃ forming MAl₂O₄ than enter into mullite structure.

The results indicate that the electrical resistivity of the composite varies from order 10¹⁰ ohm-cm at 400°C to order 10⁵ ohm-cm at 1300°C. As the temperature is increasing, the resistivity is decreasing and the activation energy initially decreases up to 0.04 M and then increases [23-25].

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2. Experimental

Mullite precursor gels are prepared from aluminium nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) extra pure (Merck, India), aluminium isopropoxide ($\text{Al}(\text{-O-i-Pr})_3$) puriss (Spectrochem Pvt. Ltd., India.), tetra ethyl orthosilicate ($\text{Si}(\text{OC}_2\text{H}_5)_4$), (Merck, Germany), Iron Nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) (MERCK Specialities Pvt. Ltd., India) and Copper sulphate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) (MERCK Specialities Pvt. Ltd., India).

For the preparation of precursor gels for mullite synthesis, $\text{Al}(\text{-O-i-Pr})_3$ and $\text{Si}(\text{OC}_2\text{H}_5)_4$ were added simultaneously to 0.5 M solution of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ dissolved in 20 ml of distilled water. The molar ratio of $\text{Al}(\text{-O-i-Pr})_3/\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was 7:2 and mole ratio of Al/Si was 3:1 [14].

Doped gels were prepared by adding corresponding metal salt to the original solution in the ratio Al:Si:M, where M is the concentration of the cobalt salt in molarity. In the final solution, M was varied as $M = 0.002$ (G_1), 0.02 (G_2), 0.10 (G_3), 0.15 (G_4) and 0.2 M (G_5) [12,13].

Gel formation was completed after stirring the solution for 3 hours and ageing the sol overnight at 60°C . The gel was then dried at 110°C and after grinding, it takes the form of freely flowing powder. The samples were then pelletized in disc form of 30 mm diameter and 3 mm thickness and sintered at 400°C , 800°C , 1000°C and 1300°C for 3 hr in a muffle furnace under air atmosphere at the heating rate of $10^\circ\text{C}/\text{minute}$ [15,18,24,25].

The fired pellets were then coated by silver paste on both sides for electrical measurements.

The silver-coated discs were placed in a press-contact type Teflon holder to minimize leakage resistance from

the holder. The chamber was made vacuum-tight and properly shielded [23-25].

3. Instrumentation

X-ray Powder Diffractometer of D8, Bruker AXS, Wisconsin, USA, using $\text{Cu K}\alpha$ radiation (1.5418 \AA) and operating at 40 KV with a scan speed of 1 s/step, analyzed phase identification of the samples sintered at 1000°C and 1300°C .

The characteristic stretching and bending modes of vibration of chemical bonds of a sample can be effectively evaluated by spectroscopic methods. 1% of the sample was mixed with spectroscopy grade KBr, pelletized and analyzed by FTIR spectroscopy (FTIR-8400S, Shimadzu).

Electrical resistivity measurements of the sintered gels were carried out by electrometer. A constant DC voltage (V) of about 1.5 V was applied from a battery across the sample. The voltage (V) across the input resistance was measured by the electrometer.

Morphology of the sintered gels were observed by Field Emission Scanning Electron Microscope (FESEM, model JSM 6700F, JEOL Ltd. Tokyo, Japan).

4. Results and Discussion

In the X-ray diffractograms, doped sintered gels shows considerable enhancement in mullite phase at 1000°C and 1300°C respectively. The sample G_0 represents undoped mullite and considerable growth of mullite has been observed at 1000°C and 1300°C respectively from the diffractograms (**Figures 1(a)** and **(b)**). The metal

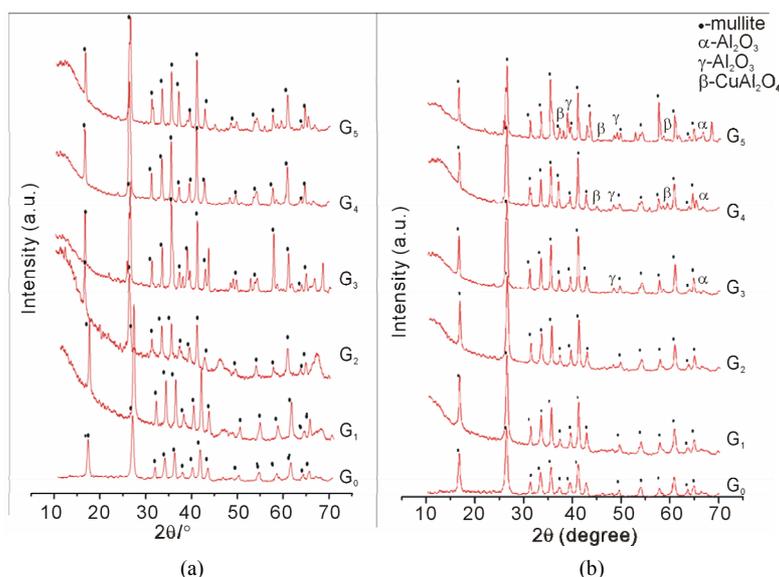


Figure 1. X-ray diffraction pattern of mullite precursor gels sintered at 1000°C and 1300°C containing increasing concentration of iron and copper ion.

cations have positive effect on the growth of mullite (JCPDS#15-776) [26] and increases with the increase of concentration of the metal ion at 1000°C and 1300°C upto G₃ (Figures 1(a) and (b)). The “mineralizing” effect of transition metals on phase transformation of mullite is well documented by other authors [16-18]. Interaction of the metal ion with the alumina and silica component of the gel is implicated in accelerated transformation to mullite phase [16,21,24,25,27]. The mineralizing effect still continues for the samples G₄ and G₅ with respect to G₀.

From the diffractograms, it was found that with the increase of metal concentration of doped metal, phase transformation in the composite increases. In the diffractograms of G₃, G₄ and G₅ samples, apart from mullite, α -Al₂O₃ (JCPDS#46-1212) [28] reflections were observed and in G₅ other metal phases are observed (Figure 1). In the higher doping concentration mullite formation slightly decreases due to the formation of aluminium oxide and metal oxides [16].

Characteristic bands at wave numbers are observed around 560, 730, 840, 1060 and 1130 cm⁻¹ (Figures 2(a) and (b)) [16]. All the characteristic bands of mullite-561 (AlO₆), 741 (AlO₄), 837 (AlO₄), 900 (AlO₄-stretching mode) and 1130 cm⁻¹ (Si-O stretching mode) appear in samples G₁, G₂, G₃, G₄ and G₅. Vibration modes corresponding to doped metal oxide bonds were observed in the FTIR spectra.

According to, Ohm’s law the current (*I*) in the circuit is

$$I = V/R, \quad (1)$$

where *V* is voltage, *I* is current, and *R* is the resistance of the load, in this case the sample of metal ion doped mullite. Therefore, the resistance (*R*) of the sample was calculated as

$$R = V/I, \quad (2)$$

In the time of measurement of resistance of each sample, the voltage of the battery was checked. The ρ resistivity of a material can be calculated using the relationship

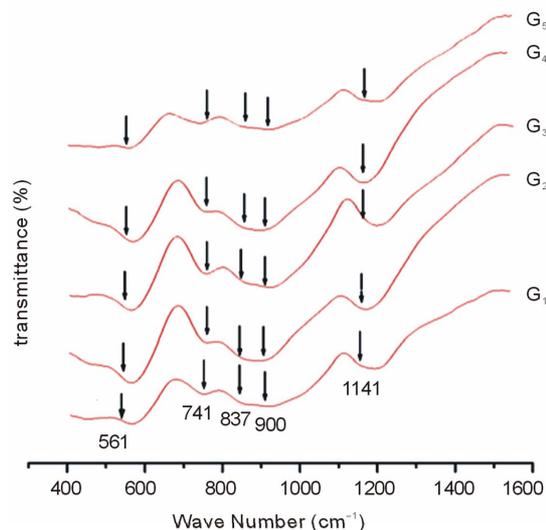
$$\rho = R(A/l), \quad (3)$$

where ρ is the material bulk resistivity, *l* is the sample length, and *A* is the sample’s cross-sectional area perpendicular to the current flow.

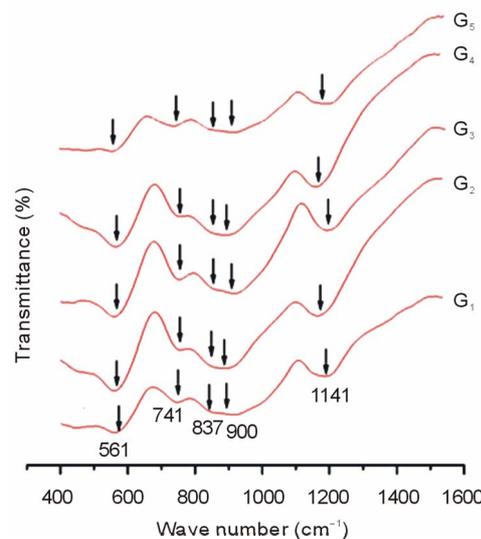
The electrical conductivity of the samples were described by the Arrhenius equation as follows

$$\sigma = \alpha e^{E_g/kT}, \quad (4)$$

where σ is the electrical conductivity given by $\sigma = 1/\rho$, α is a pre-exponential factor, *T* is the absolute temperature, *k* is the Boltzmann constant, and *E_g* is the material’s activation energy.



(a)



(b)

Figure 2. FTIR bands of mullite precursor gels sintered at 1000°C and 1300°C containing increasing concentration of iron and copper ion.

The electrical resistivity of the samples were described as

$$\rho = 1/\sigma, \quad (5)$$

where ρ is the material bulk resistivity and σ is the electrical conductivity [23-25].

A plot of log₁₀ ρ versus $1/T \cdot 10^4$ was drawn for each sample at temperatures 400°C, 800°C, 1000°C and 1300°C (Figures 3(a) and (b)). The plots show a linear increase with the reciprocal temperature.

From the log₁₀ ρ vs sintering temperature (°C) curve (Figures 4(a) and (b)), resistivity decreases with increasing temperature. It has been observed that for con-

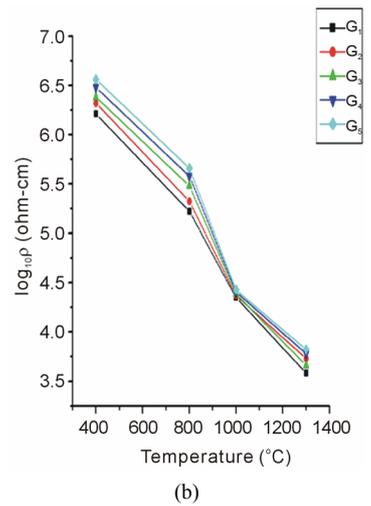
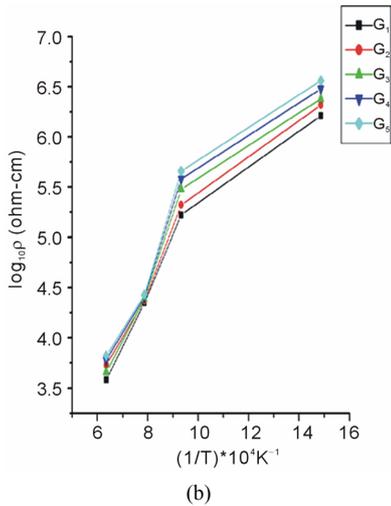
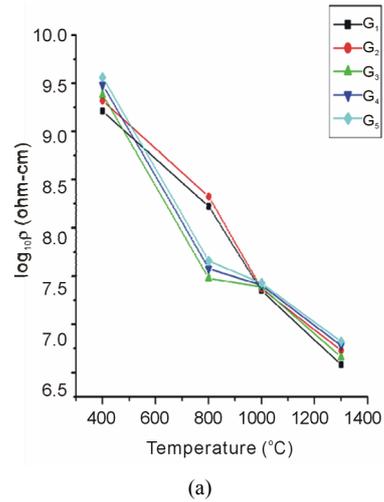
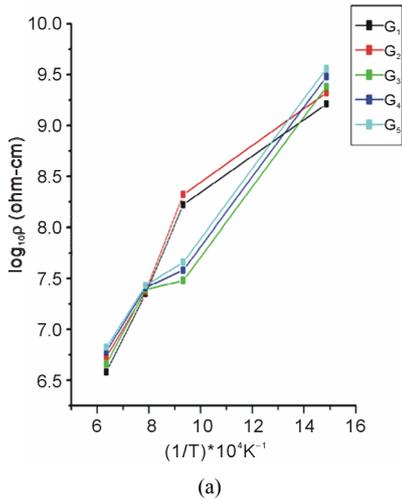


Figure 3. Resistivity ($\log_{10} \rho$) versus $1/T * 10^4$ graph of mullite precursor gels sintered at 400°C, 800°C, 1000°C and 1300°C containing increasing concentration of iron and copper ion.

Figure 4. Resistivity versus Temperature (°C) of mullite precursor gels sintered at 400°C, 800°C, 1000°C and 1300°C containing increasing concentration of iron and copper ion.

centration G_1 and G_2 the resistivity decreases sharply in the higher temperature range, but in the lower temperature range G_3, G_4, G_5 decrease rapidly. G_1 exhibits the lowest resistivity $6.57 \times 10^5 \Omega \text{ cm}$ for Fe^{2+} and $3.56 \times 10^5 \Omega \text{ cm}$ for Cu^{2+} . The Fe^{2+} and Cu^{2+} ions react with Al_2O_3 forming metal aluminates and other phases and responsible for decreasing resistivity with sintering temperature.

The activation energy of the samples was calculated in eV unit from the slope of the plot as follows:

$$E_g = \text{slope} \times 4.606 \times 8.62 \times 10^{-5} \text{ eV} \quad [23-25]. \quad (6)$$

From the E_g vs concentration curve, E_g decreases with concentration and becomes minimum at 0.04 M for Cu^{2+} ion concentration (**Figure 5**).

The substitution of Al^{3+} ion in the mullite lattice by Fe^{2+} and Cu^{2+} ion hampered the electro neutrality of the composite. As a result probably there will be formation

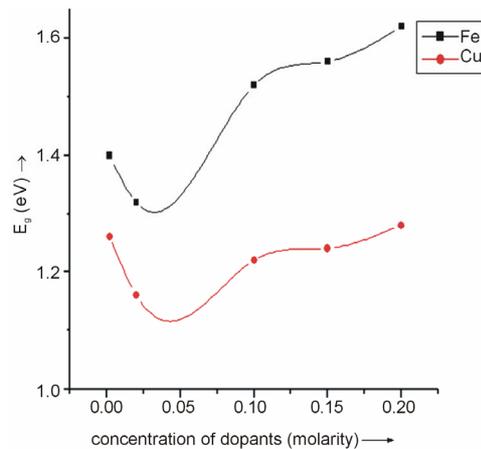


Figure 5. Activation energy (E_g) vs concentration curve of mullite precursor gels sintered at 400°C, 800°C, 1000°C and 1300°C containing increasing concentration of iron and copper ion.

of a hole when Al^{3+} ion is replaced by Fe^{2+} and Cu^{2+} ion in the mullite structure [23-25]. It was observed that Fe^{2+} and Cu^{2+} ion could not substitute Al^{3+} ion in mullite but remained there as a cluster. The lowering of resistivity is due to the 3d orbital electrons and the concentration of metal ions. The Fe^{2+} and Cu^{2+} ion which substituted Al^{3+} ion in the octahedral site of mullite structure appeared to be efficient in reducing the resistivity [23-25]. There are two possibilities of increase of E_g after attaining its minimum value at 0.04 M for Cu^{2+} , either complete incorporation of Cu^{2+} ion in the mullite structure or dissolution of copper ions in the Si-rich glassy phase. The dissolution of metal ions in the glassy phase should dominate over the incorporation of metal ions into mullite.

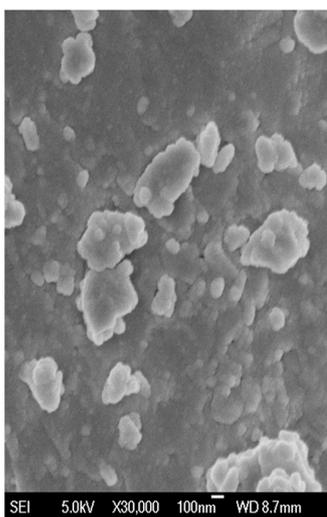
Mullite samples, therefore, behave like nonmetallic

electrical conductors, because their conductivity rises faster at lower temperature but slows down at higher temperature.

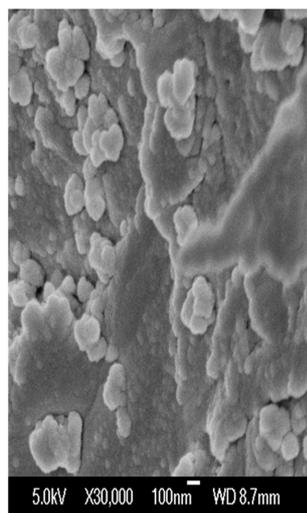
The morphology of mullite particles with lowest (G_1) and highest (G_5) concentrations of Fe^{2+} and Cu^{2+} ion sintered at $1000^\circ C$ and $1300^\circ C$ was investigated by FESEM.

The micrograph for G_1 shows almost round particles of mullite of an average size of 200 nm. Numerous smaller particles can also be seen along with amorphous aggregates (**Figures 6(a) and (b)**) [12,29-31].

G_5 samples shows distinct acicular morphology of mullite crystals of size 600 nm embedded in the matrix (**Figures 7(a) and (b)**). The mullite content and crystallization in all the G_5 samples were greater than in G_1 composites, indicating the catalytic effect of the Fe^{2+} and Cu^{2+} ions [16,24,25].

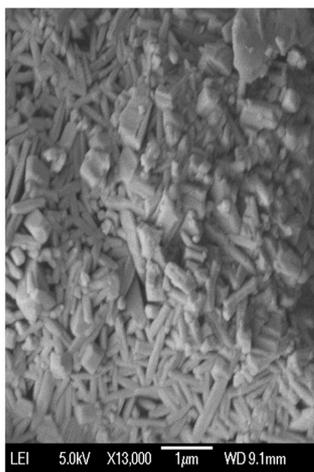


(a)

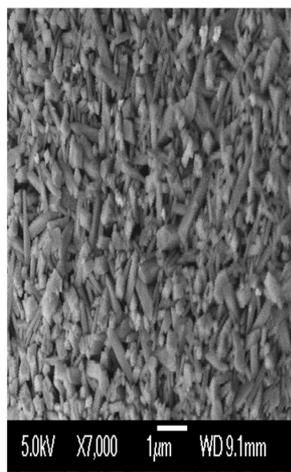


(b)

Figure 6. FESEM of mullite precursor gels doped with iron and copper ion sample G_1 sintered at $1000^\circ C$ and $1300^\circ C$.



(a)



(b)

Figure 7. FESEM of mullite precursor gels doped with iron and copper ion sample G_5 sintered at $1000^\circ C$ and $1300^\circ C$.

5. Conclusion

Fe²⁺ and Cu²⁺ doped mullite composites have been synthesized by the sol-gel technique, their phase evolution; band gap activation energy has been investigated. The results showed that with increase in Fe²⁺ and Cu²⁺ ion concentration the crystallization of mullite was enhanced, which is evident from X-ray diffraction and FESEM of the composites. The activation energy of resistivity/band gap energy, *E_g*, attains a minimum value 1.11 eV at 0.04 M concentration for Cu²⁺ ion. It has been observed that the resistivity as well as the band gap energy corresponds to semiconductors and due to the low activation energy it can be used as a substrate in the electronic industry.

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