

# STUDY OF DENSIFICATION OF SOL-GEL DERIVED MULLITE DUE TO EXCESS IRON, NICKEL AND COPPER IONS

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Submitted January 10, 2013; accepted October 6, 2013

**Keywords:** Densification, Sol-gel processes, Nanocomposite, Scanning electron microscopy (SEM), X-ray diffraction (XRD)

*Mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) samples doped with 0.4 M, 0.6 M, 0.8 M, 1.0 M and 1.2 M of iron, nickel and Copper, were prepared by a sol-gel process. Prepared gels were then dried, grinded, pressed into pellets and sintered at temperatures 1100°C and 1400°C for 4 h. Phase formation, densification behavior has been investigated as a function of the metal content and sintering temperature. The density of the sintered ceramics was measured using Archimedes method.*

*The main intention is to study the role of metal ions in influencing mullitization behavior in the case of the sol-gel reaction process, in order to provide useful information of mullite. This paper deals with the effect of metal ions on mullite formation, microstructure and densification behavior in single-phase sol-gel derived mullite. The results showed with increase in concentration of metals ( $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ), crystallization of mullite was enhanced which is evident from X-ray diffraction upto  $G_3$  and FESEM of the composites. The density of the doped samples increases with the increase of metal ion concentration as well as with the sintering temperature. Copper-doped mullite exhibits the highest density  $2.46 \text{ g cm}^{-3}$  at 1400°C.*

## INTRODUCTION

Mullite is a highly stable ceramic material with high mechanical strength, low dielectric constant, high creep resistance and low thermal expansion coefficient at high temperatures mullite ceramic is widely used as a structural and refractory ceramic material. Mullite is a widely used ceramic for structural applications because of its high melting point, good chemical, thermal stability, and excellent high-temperature strength [1-8]. Generally, mullite formation starts from 1000°C and is completed at about 1600°C, due to solid-state reaction between  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  particles [4-10].

Mullite formation is related not only to material processing but also to introduction of other compounds, especially oxides. Our intention is to study the role of transition metal ions in influencing mullitization behavior in the case of the sol-gel reaction process, in order to provide useful information of mullite or mullite related materials [10, 12]. The effect of metal ions on mullite formation, microstructure and densification behaviour, in single-phase sol-gel derived mullite precursor is reported in this paper.

## EXPERIMENTAL

Chemicals used in the preparation of mullite precursor gels are Aluminium nitrate nonahydrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), Aluminium isopropoxide ( $\text{Al}(\text{-O-i-Pr})_3$ ), Tetra ethyl orthosilicate ( $\text{Si}(\text{OC}_2\text{H}_5)_4$ ), Iron Nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), Nickel chloride hexahydrate ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ) and Copper sulphate pentahydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ). For the preparation of the 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 0.5M 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 [10-13]. The metal salts were added to the original solution so that concentration of the metal salt in molarity will be 0.4 M ( $G_1$ ), 0.6 M ( $G_2$ ), 0.8 M ( $G_3$ ), 1.0 M ( $G_4$ ) & 1.2 M ( $G_5$ ).

Gel formation was complete after stirring the solution for 4 hours and ageing the sol overnight at 60°C. The gel was then dried at 110°C and finely ground to powder form. The samples were then palletized and sintered at 1100°C and 1400°C for 2 hrs in a muffle furnace under air atmosphere (heating rate 10°C/min.) [10-13].

Phase identification of the samples sintered at 1100°C and 1400°C was analyzed by X-ray Powder Diffractometer (model-D8, Bruker AXS, Wisconsin, USA) using Cu K $\alpha$  radiation - 1.5418 Å and operating at 40 kV with a scan speed of 1 sec/step.

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

Morphology of the sintered gels was observed by Field Emission Scanning Electron Microscope (FESEM) (JSM 6700F, JEOL Ltd. Tokyo, Japan) at an accelerating voltage of 5.0 kV and a working distance of 7 to 8 mm. Powdered samples were etched with 25 % HF solution. About 2 mg of each sample was dispersed in ethanol and a single drop was placed on copper grid for sample preparation.

Density of the samples was determined by using displacement method (Table I). According to Archimedes principle the density of the sample  $\rho = m/V$ , where  $m$  is the mass of the sample and  $V$  is the volume as determined by the displacement method. [13].

## RESULTS AND DISCUSSION

It can be seen from the XRD analysis that the undoped sample ( $G_0$ ) shows considerable mullite phase at 1100°C (Figure 1) and at 1400°C (Figure 2), while for the doped samples mullite phase changes with changing concentration of metal ions. All the metal ions had positive effect on the growth of mullite (JCPDS#15-776) [14]. Mullite phase increases with increasing concentration of metal ions upto  $G_3$  and as well as with temperature. The ‘mineralizing’ effect still continues for samples  $G_4$  and  $G_5$  with respect to control sample  $G_0$ . In the higher doping ion concentrations ( $G_4$  and  $G_5$ ) enhancement of mullite formation slightly decreases, because aluminium ion ( $Al^{3+}$ ) is being used up for the formation of other phases (aluminium oxide and metal aluminates). The phase variation of the composite was due to the changed concentration of each metal ion and was because of Jahn-Teller Distortion [2, 10, 12, 21]. The observed difference in mullite formation (Figure 1 a), b), c) of metal ions was due to weak ligand field. For weak ligand field the metal ions will be in high spin configuration. Interaction of

the metal ions with the alumina and silica component of the gel is responsible for the accelerated transformation to mullite phase [11-12, 21]. The content of crystalline mullite decreases and the background increases due to the increase of metal ion concentration and due to the formation of metal silicate and aluminate phases of the samples. The ‘mineralizing’ effect continues for samples  $G_4$  and  $G_5$  with respect to control sample  $G_0$ . The ‘mineralizing’ effect of transition metals on phase transformation of mullite is well documented by authors [2, 10-12, 21]. Probably there are two possibilities, either complete incorporation of metal ions in mullite structure or dissolution of metal ions in the Si- rich glassy phase. As such amorphous phase increases with the increased metal ions, as an account of decrease of the crystalline phases. The densification of the composite may be due to increased consolidation of the composite because of the molten state of the sintered gel at 1400°C (Figure 7) and for the increasing metal ion concentration.

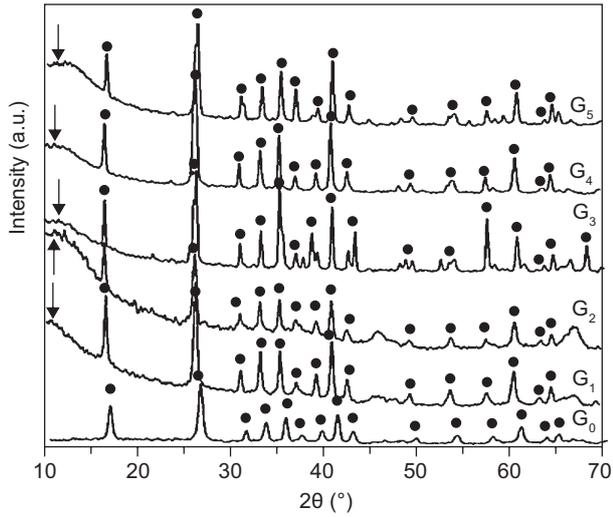
Mullite (prepared using KBr disc method) sintered at temperatures 1100°C and 1400 °C, gives characteristic bands at wave numbers around 560, 730, 840, 1060, 1130 and 1170  $cm^{-1}$ [11,12]. Figure 3 (1100°C) and Figure 4 (1400°C) shows the FTIR spectra of the sintered gels. All the characteristic bands of mullite- 561 ( $AlO_6$ ), 741 ( $AlO_4$ ), 837 ( $AlO_4$ ), 900 ( $AlO_4$  stretching mode) and 1141  $cm^{-1}$  (Si–O stretching mode) appear in all the doped samples of 1100°C sintered gels, but 900( $AlO_4$  stretching mode) is not obtained, but rest of the bands are obtained in all doped samples of 1400°C sintered gels [15-16, 21].

The densities of all the concentration of doped metal composites were determined. It has been observed that as doping concentration increases density also increases. Experimental data also shows that the samples density also increases with the increase of temperature (Table 1). Iron ion doped mullite ( $G_1$ ) is having lowest density at 1100°C; it is 1.64  $g/cm^3$  and copper ion doped mullite ( $G_5$ ) exhibits maximum density at 1400°C; it is 2.46  $g/cm^3$  (Table 1). From X-ray Diffraction and FESEM, it can be seen that mullite content increases with doping concentration upto  $G_3$ .

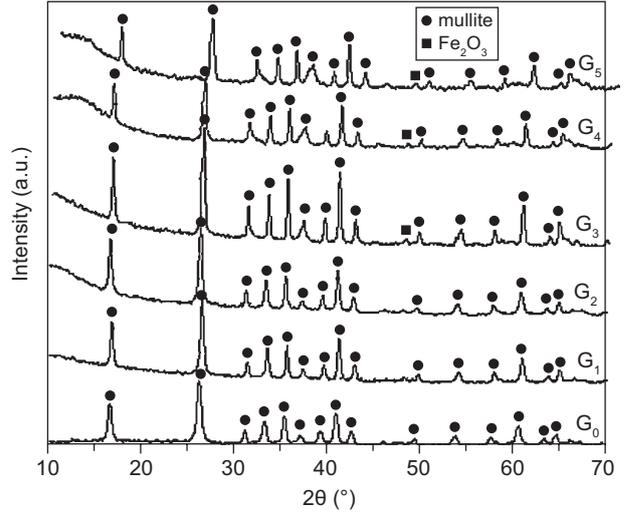
The morphology of the mullite particles of lowest ( $G_1$ ) and highest ( $G_5$ ) concentration of the doped metals were investigated by FESEM. The micrograph for  $G_1$  shows round shaped particles of mullite of average size 250 nm and for  $G_5$  distinct morphology of cylindrical structure of mullite particles of size 300 nm for the samples sintered at 1100°C. Numerous particles can also be seen along with amorphous aggregates. [2, 5] (Figure 6).

Table 1. Density of samples ( $g/cm^3$ ).

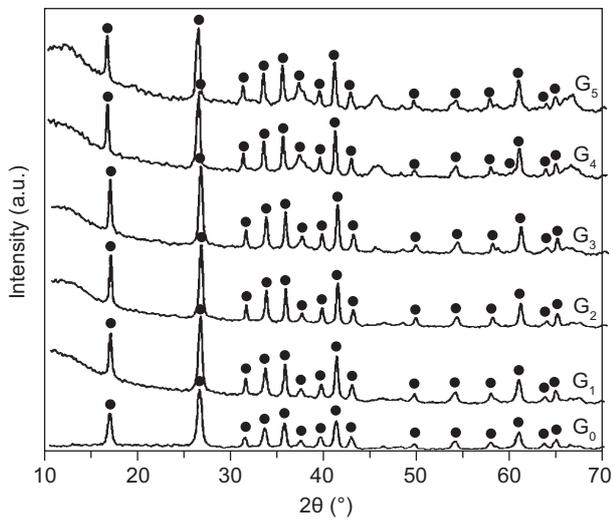
Samples at 1100°C/1400°C	$G_0$	$G_1$	$G_2$	$G_3$	$G_4$	$G_5$
Iron doped mullite	1.60/1.62	1.64/1.66	1.68/1.70	1.68/1.72	1.70/1.72	1.74/1.76
Nickel doped mullite	1.60/1.62	1.84/ 1.89	1.88/1.91	2.02/2.04	2.05/2.08	2.14/2.24
Copper doped mullite	1.60/1.62	1.94/1. 98	1.98/2.06	2.12/2.28	2.24/2.36	2.39/2.46



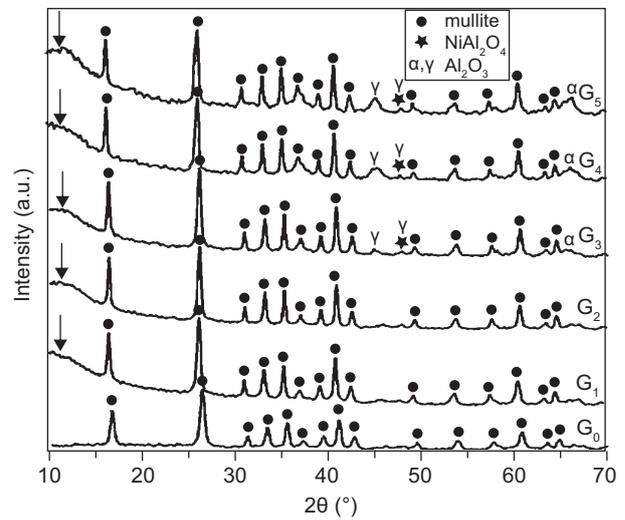
a) Fe (1100°C)



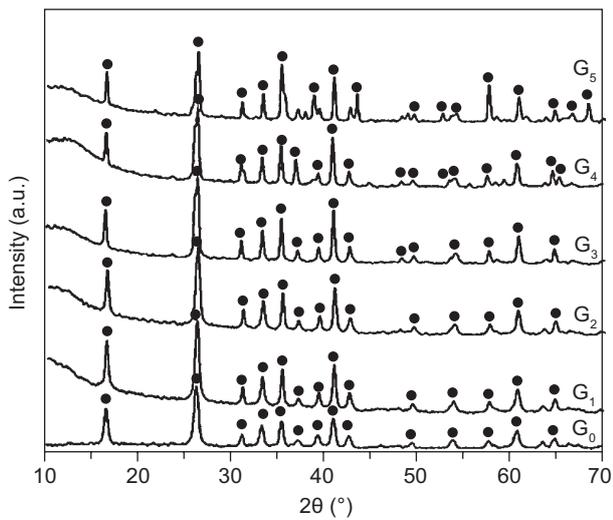
a) Fe (1400°C)



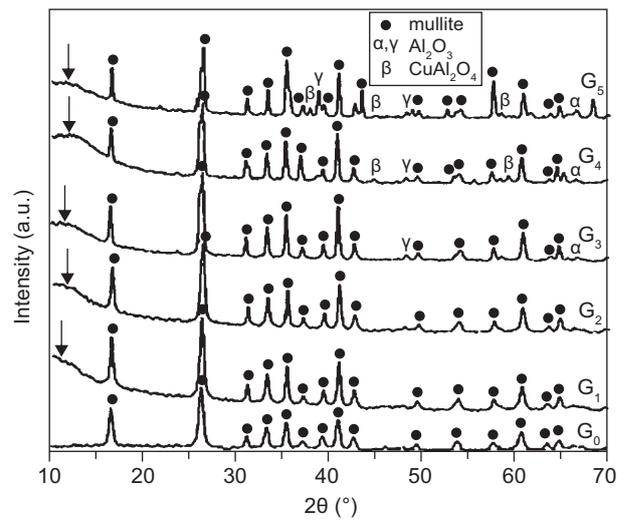
b) Ni (1100°C)



b) Ni (1400°C)



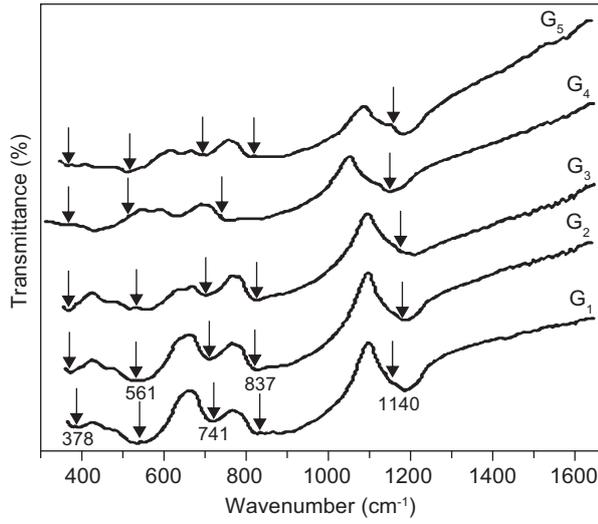
c) Cu (1100°C)



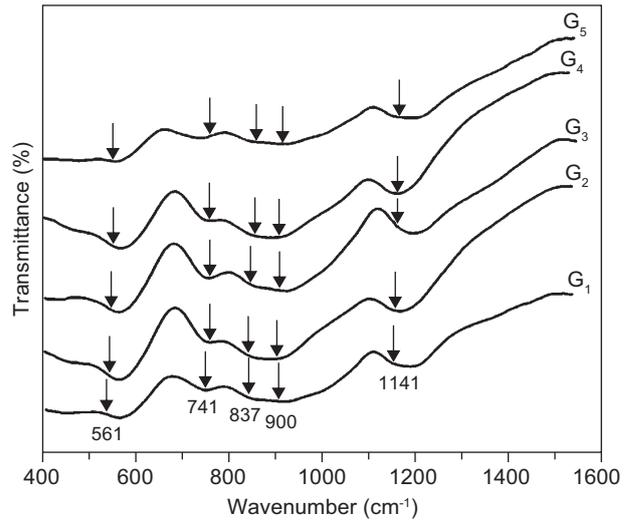
c) Cu (1400°C)

Figure 1. X-ray diffraction pattern of mullite precursor gels sintered at 1100°C containing increasing concentration of metal ions.

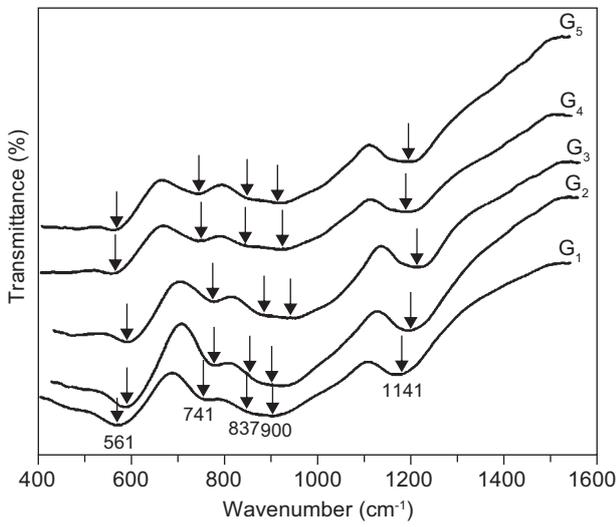
Figure 2. X-ray diffraction pattern of mullite precursor gels sintered at 1400°C containing increasing concentration of metal ions.



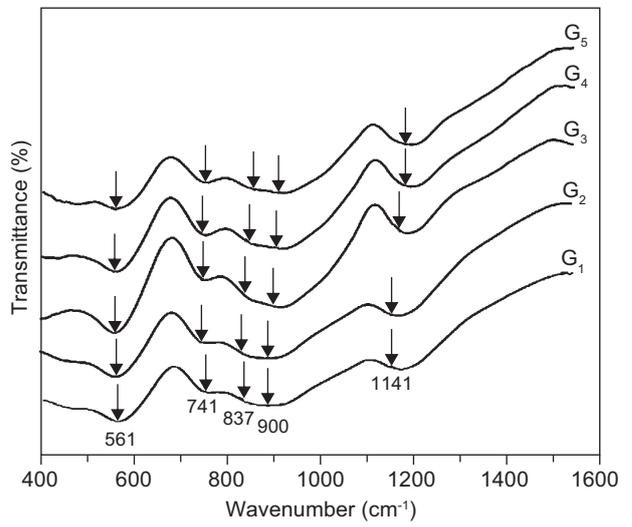
a) Fe (1100°C)



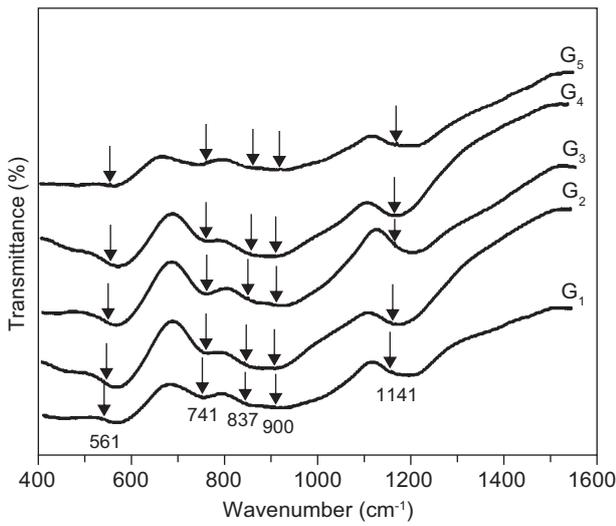
a) Fe (1400°C)



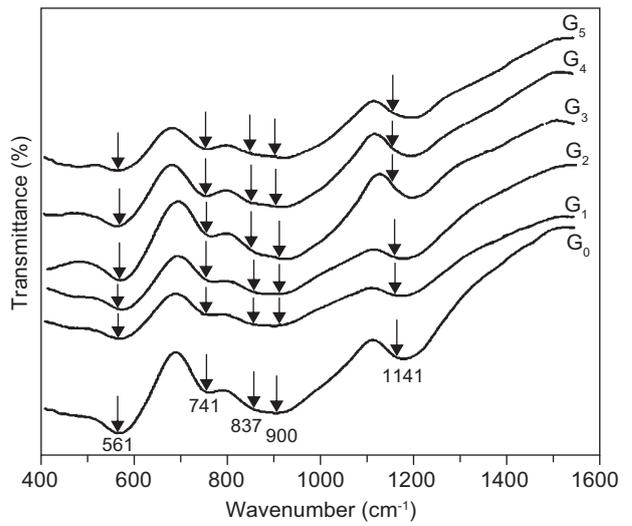
b) Ni (1100°C)



b) Ni (1400°C)



c) Cu (1100°C)



c) Cu (1400°C)

Figure 3. FTIR micrograph of sample G<sub>1</sub>, G<sub>2</sub>, G<sub>3</sub>, G<sub>4</sub> and G<sub>5</sub> sintered gels at 1100°C for 3 hrs for metal ions.

Figure 4. FTIR micrograph of sample G<sub>1</sub>, G<sub>2</sub>, G<sub>3</sub>, G<sub>4</sub> and G<sub>5</sub> sintered gels at 1400°C for 3 hrs for metal ions.

The micrograph for the samples sintered at 1400°C shows molten structure (Figure 7). As a result of increase in sintering temperature the cylindrical structure is destroyed and it shows the plate like structure. The mullite content and crystallization in all the G<sub>5</sub> samples were greater than in G<sub>1</sub> composites indicating the catalytic effect of the metal ions at 1100°C and 1400°C. [17-21]

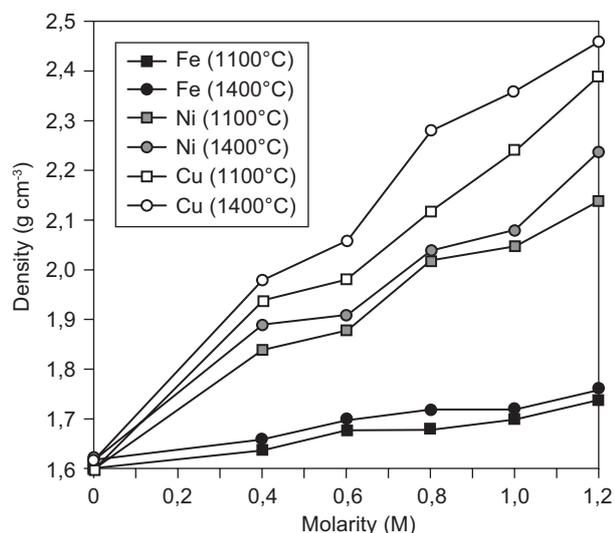


Figure 5. Density of the samples with metal ions concentration of mullite in samples sintered at 1100°C and 1400°C.

## CONCLUSION

Iron, nickel and copper-doped mullite composites have been synthesized by sol-gel technique. The metal ion concentrations are 0.4 M, 0.6 M, 0.8 M, 1.0 M and 1.2 M of iron, nickel and Copper. The phase evolution and microstructure has been investigated and the results showed an increase in mullite phase up to G<sub>3</sub> and glassy phase continued to increase with doping concentration.

The mullite phase formation is accelerated due to metal ion doping upto a certain concentration, and then after G<sub>3</sub> we can assume formation of amorphous glassy phase. The mullite content increases with the increase of metal concentration, but the mullite content is maximum for the addition of nickel.

The addition of nickel was advantageous for the densification of mullite. The sample density increases with sintering temperature and metal ion incorporation.

## Acknowledgement

We are grateful to DST and UGC (PURSE program), Government of India, for their support and grateful to Dr.R.N.Basu for his constant help in completing the work.

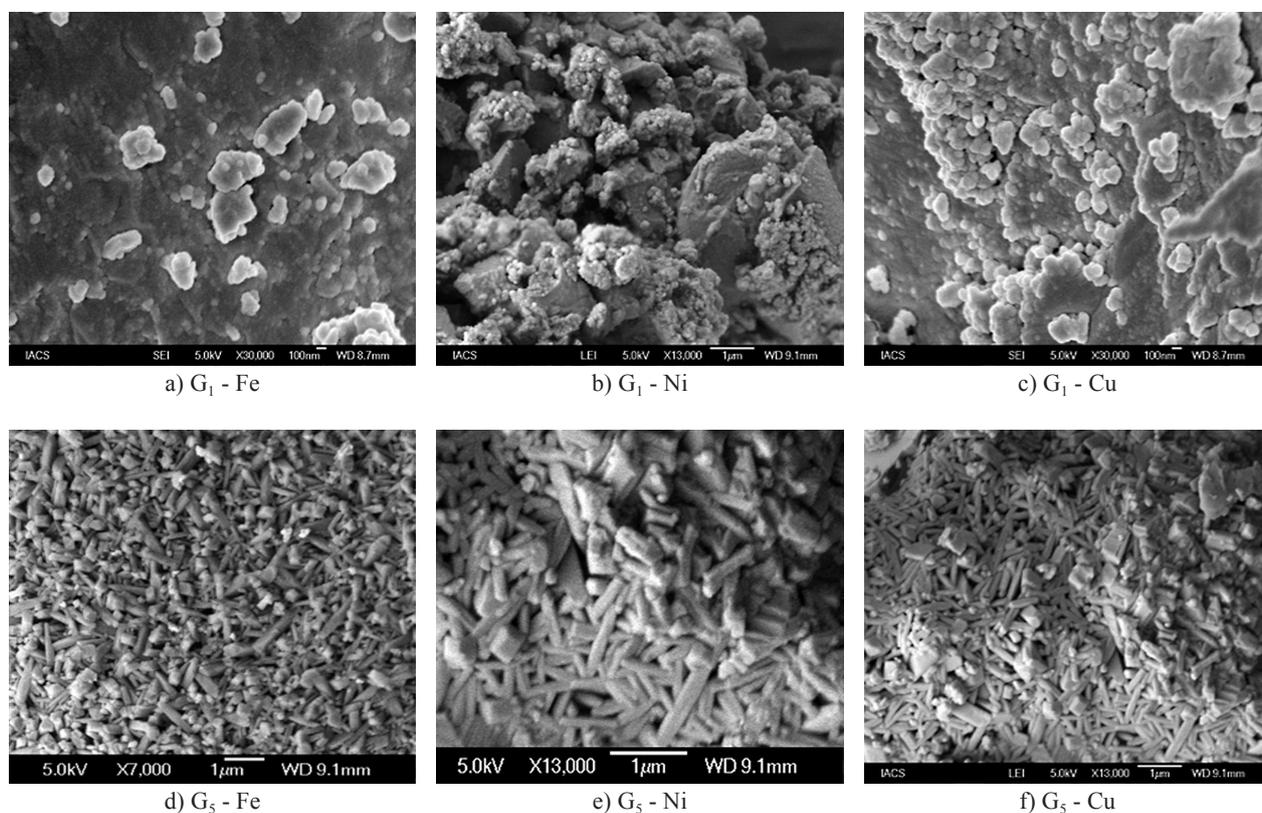


Figure 6. FESEM of mullite precursor gels doped with metal ions for sample G<sub>1</sub> and G<sub>5</sub> sintered at 1100°C.

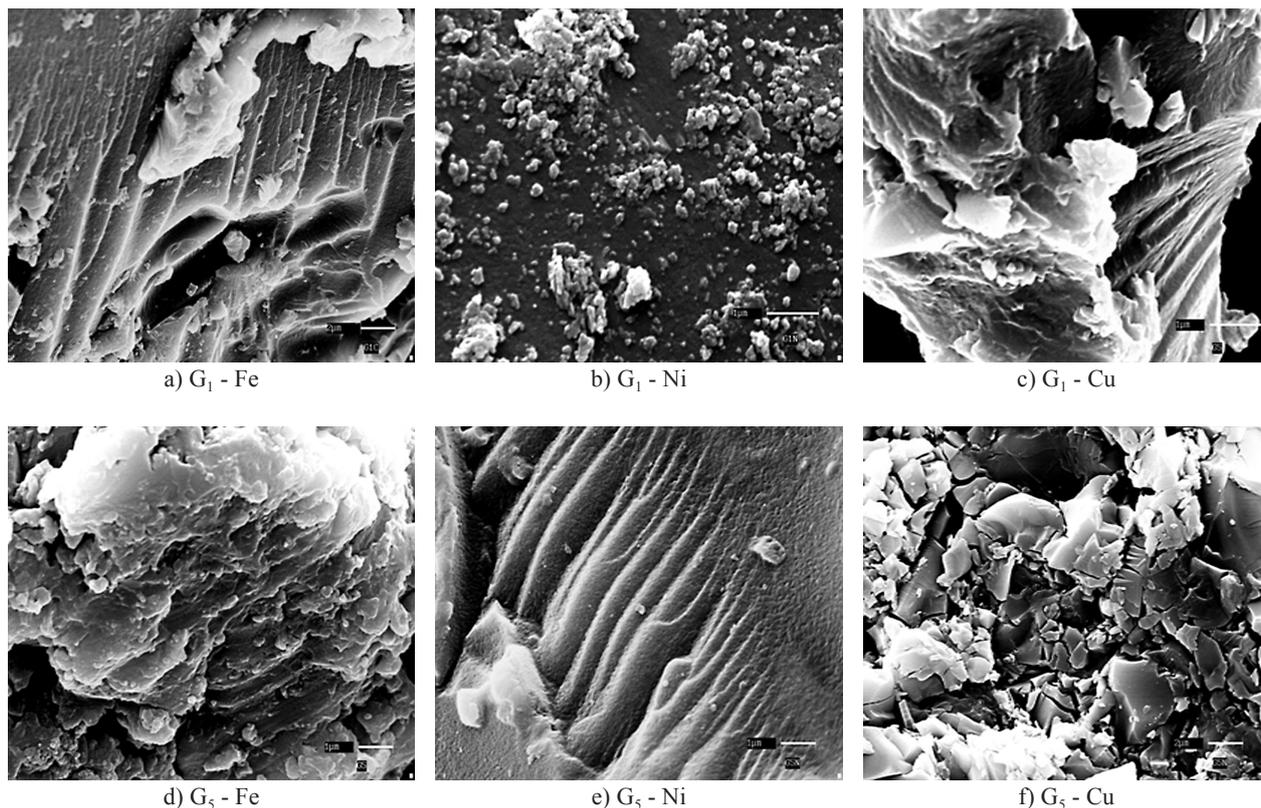


Figure 7. FESEM of mullite precursor gels doped with metal ions for sample G<sub>1</sub> and G<sub>5</sub> sintered at 1400°C.

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