

Possibility of decreasing the activation energy of resistivity of mullite by doping with nickel ion

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Monophasic mullite samples doped with 0.002 M, 0.02 M, 0.1 M, 0.15 M and 0.2 M of NiCl_2 were prepared via sol-gel technique. The prepared gels were dried, grinded, pressed into pellets and sintered at 400 °C, 800 °C, 1000 °C and 1300 °C. The electrical resistivity and activation energy of the composites have been measured and the variation of resistivity with concentration of the nickel ion doping has been investigated. The resistivity decreases with the concentration of nickel ions. X-ray analysis confirms the presence of Ni^{2+} ions in mullite. The Ni^{2+} ion, which substitutes Al^{3+} ion in the octahedral site of mullite structure, can be considered as an efficient factor in reducing the resistivity. The mullite unit cell parameters suggest predominant incorporation of NiCl_2 in a glassy phase. The lowest activation energy of resistivity (E_{act}) that was achieved is 1.22 eV at 0.02 M.

Keywords: nanocomposite; sol-gel methods; scanning electron microscopy (SEM); X-ray diffraction (XRD); electrical resistivity

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1. Introduction

Mullite is an important high-technology ceramics for high temperature applications. It has high mechanical strength, low thermal expansion coefficient, low dielectric constant and high creep resistance [1–9]. Generally, mullite formation starts from 1000 °C and is completed at about 1600 °C, due to a solid-state reaction between Al_2O_3 and SiO_2 particles [10–16]. Synthesis of mullite composites in the presence of various doping agents modifying the mechano-chemical properties has been reported by many authors, however, the literature items concerning the activation energy of resistivity (E_{act}) of nickel doped mullite composites are relatively few [16–23].

This paper deals with the synthesis of mullite composites doped with varying concentrations of nickel ions and determines the effect of the concentration on the activation energy of resistivity of the composites at temperatures of 400 °C, 800 °C, 1000 °C and 1300 °C. It has been observed that the electrical resistivity of a composite varies with the variation of temperature. As the temperature is increasing, the resistivity is decreasing [24, 25].

The lattice parameters (a , b , c) and unit cell volume change due to the incorporation of nickel ion. Synthesis of mullite composites in the presence of various doping agents has shown that these changes in structural parameters do not depend on the nature of the dopants [26, 28]. The parameters of undoped mullite ($a = 0.7544$ nm, $b = 0.7687$ nm and $c = 0.2881$ nm and unit cell volume 0.16707 nm³) [25] change due to the doping with nickel ions at 1300 °C. It has been observed that the dimension along a axis does not change, along b axis contraction takes place whereas the dimension in c axis increases steadily.

2. Experimental

The samples used in the experiments were extra pure aluminium nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Merck, India), aluminium isopropoxide ($\text{Al}(\text{O}-i\text{-Pr})_3$, puriss Spectrochem Pvt. Ltd., India.), tetra ethyl orthosilicate ($\text{Si}(\text{OC}_2\text{H}_5)_4$, Merck, Germany) and nickel chloride hexahydrate ($(\text{NiCl}_2 \cdot 6\text{H}_2\text{O})$, Merck Specialities Pvt. Ltd., India). For the preparation of precursor gels for mullite synthesis, $\text{Al}(\text{O}-i\text{-Pr})_3$ 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 cm³ of distilled water. The molar ratio

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of $\text{Al}(-\text{O}-i\text{-Pr})_3/\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was 3.5 and the mole ratio of Al/Si was 3:1 [15]. Doped gels were prepared by adding $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ to the original solution. The molar ratio of $\text{Al}:\text{Si}:\text{Ni}$ was varied as 0.5: 1.75: M , with $M = 0.002(\text{G}_1)$, $0.02(\text{G}_2)$, $0.10(\text{G}_3)$, $0.15(\text{G}_4)$ and $0.2\text{ M}(\text{G}_5)$ [13–15]. After stirring the solution for 3 hours, the gel formation was completed. The solution was then kept overnight at 60°C . The gel was then dried at 110°C and after grinding, it took the form of freely flowing powder. The samples were then pelletized in a disc form and sintered at 400°C , 800°C , 1000°C and 1300°C for 3 h in a muffle furnace under air atmosphere at the heating rate of $10^\circ\text{C}/\text{min}$. [16–20]. The fired pellets were then coated with 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 [25]. 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 with an electrometer.

X-ray powder diffractometer D8 (Bruker) using $\text{CuK}\alpha$ radiation (1.5418 \AA) and operating at 40 kV with a scan speed of 1 s/step, was used for phase identification of the samples sintered at 400°C , 800°C , 1000°C and 1300°C and the pattern refinements were obtained by the Rietveld method, using the FullProf software. The characteristic stretching and bending modes of vibration of chemical bonds of a sample can be effectively evaluated by spectroscopic methods (FTIR-8400S, Shimadzu). Electrical resistivity measurements of the sintered gels were carried out with an electrometer. Morphologies of the sintered gels were observed by Field Emission Scanning Electron Microscope (FESEM, model JSM 6700F, JEOL Ltd. Tokyo, Japan).

3. Results and discussion

X-ray diffractograms of doped sintered gels show considerable enhancement in mullite phase at 800°C , 1000°C and 1300°C respectively. The metal cation Ni^{2+} has a positive effect on the growth of mullite (JCPDS#15-776) [29] and results in the enhanced growth with the increase of

concentration of the nickel ion at 800°C , 1000°C and 1300°C (Fig. 1a–e). Authors [17–20] documented the effect of transition metals on phase transformation of mullite. Interaction of the metal ion with the alumina and silica component of the gel helped in accelerated transformation to mullite phase [17, 23, 28]. It has been found that with the increase of metal ion concentration, phase transformation in the composite increases. In the diffractograms of G_3 , G_4 and G_5 samples, apart from mullite, $\alpha\text{-Al}_2\text{O}_3$ (JCPDS#46-1212) [30] reflections are observed and in G_5 sample, nickel doped NiAl_2O_4 (JCPDS# 10-0339) [31] phases can be recognized (Fig. 1e). Characteristic bands are observed at wave numbers around 560, 730, 840, 900 and 1140 cm^{-1} (see Fig. 2a–e) [17, 18]. All the characteristic bands of mullite – 561 (AlO_6), 741 (AlO_4), 837 (AlO_4), 900 (AlO_4 – stretching mode) and 1130 cm^{-1} (Si–O stretching mode) appear in samples G_1 , G_2 , G_3 , G_4 and G_5 . These are characteristic bands of mullite phase as reported by Oreefice and Vasconcelos [18]. There is no band around 1380 cm^{-1} or 1630 cm^{-1} , indicating the removal of volatile components. The resistivity (ρ) of the samples,

$$\rho = R(A/l) \quad (1)$$

where R , A and l are the resistance, area of cross-section and thickness of the sample.

Using the Arrhenius equation, the electrical resistivity of the samples was determined as:

$$\rho = \rho_0 \exp[E_{act}/(kT)] \quad (2)$$

where ρ and ρ_0 are the resistivities of the samples at arbitrary temperature and 0°C , respectively. E_{act} , k and T are activation energy of resistivity, Boltzmann constant and absolute temperature, respectively [25–27]. The $\log_{10}\rho$ versus $1/T \times 10^4$ was drawn for each sample at temperatures 400°C , 800°C , 1000°C and 1300°C (see Fig. 3).

From the $\log_{10}\rho$ versus sintering temperature curve (Fig. 4), it can be observed that, for all concentrations, resistivity decreases steadily in the lower temperature range, but decreases rapidly in the higher temperature range. The activation energy of the samples was calculated in eV units from the slope of the plot as follows [25]:

$$E_{act} = \text{slope} \times 2.303 \times 8.62 \times 10^{-5} \text{ eV} \quad (3)$$

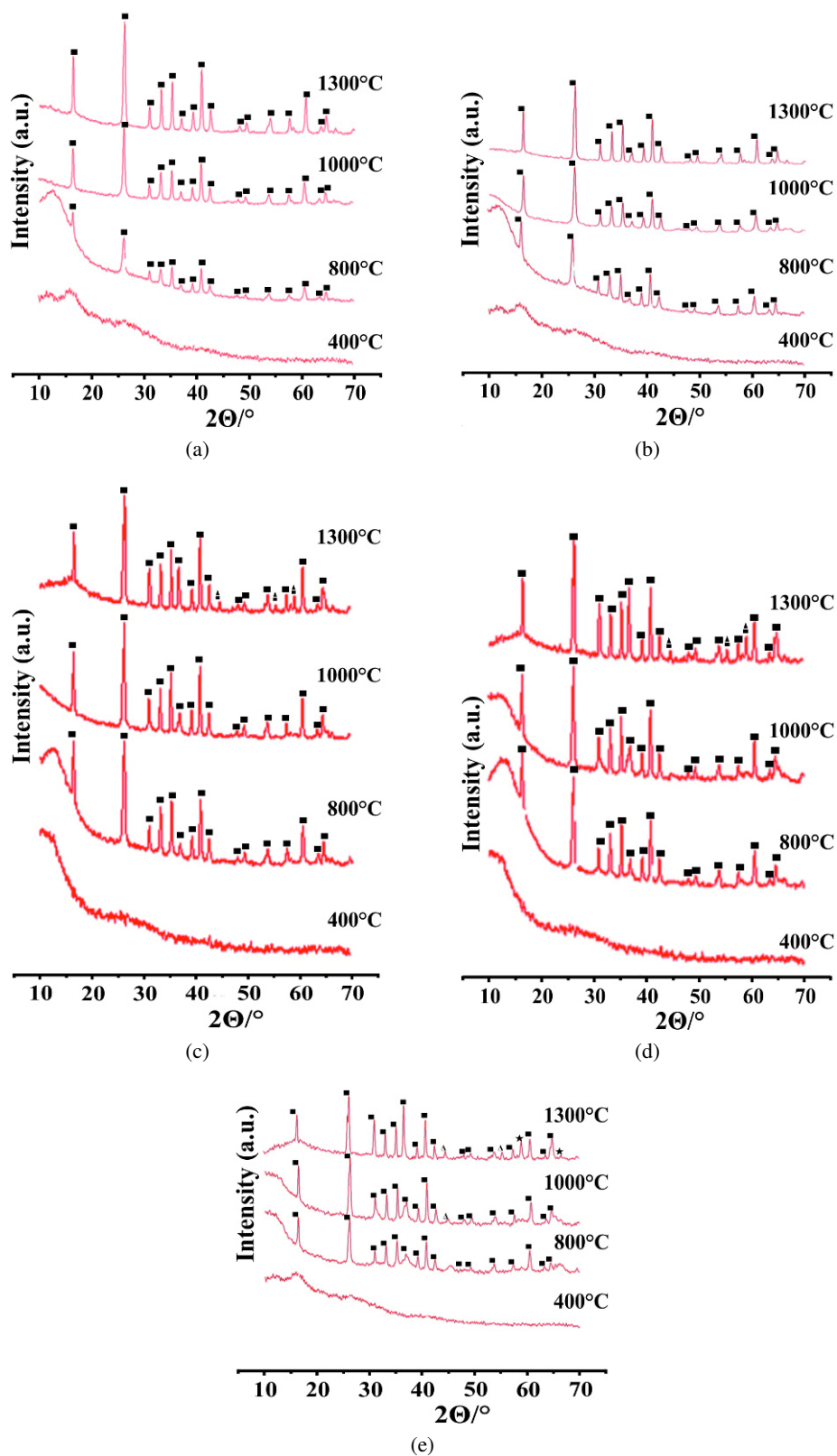


Fig. 1. X-ray diffraction patterns of mullite precursor gels containing increasing concentration of nickel: a) G₁, b) G₂, c) G₃, d) G₄ and e) G₅, sintered at 400 °C, 800 °C, 1000 °C and 1300 °C.

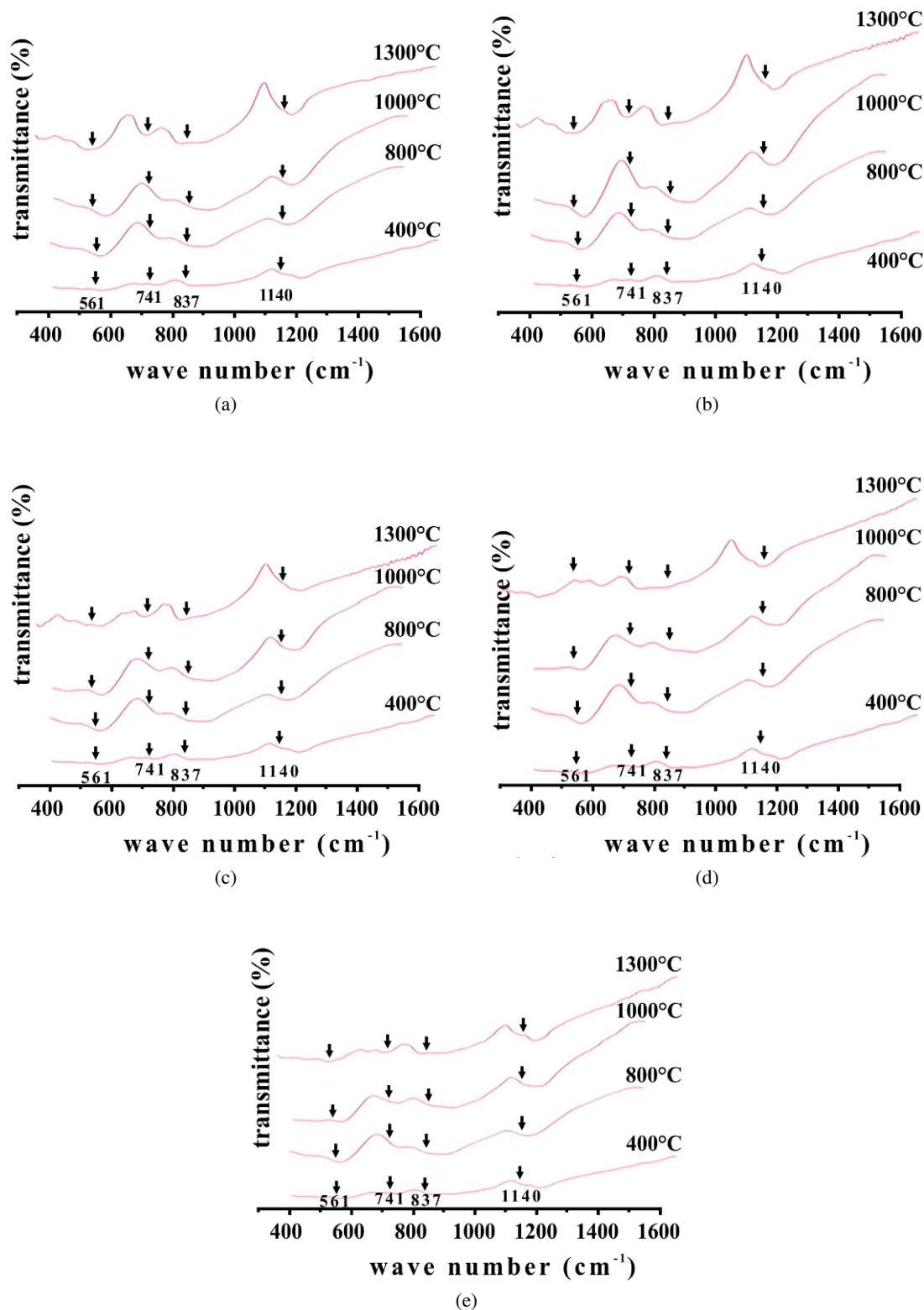


Fig. 2. FTIR bands of mullite precursor gels containing increasing concentration of nickel: a) G₁, b) G₂, c) G₃, d) G₄ and e) G₅, sintered at 400 °C, 800 °C, 1000 °C and 1300 °C.

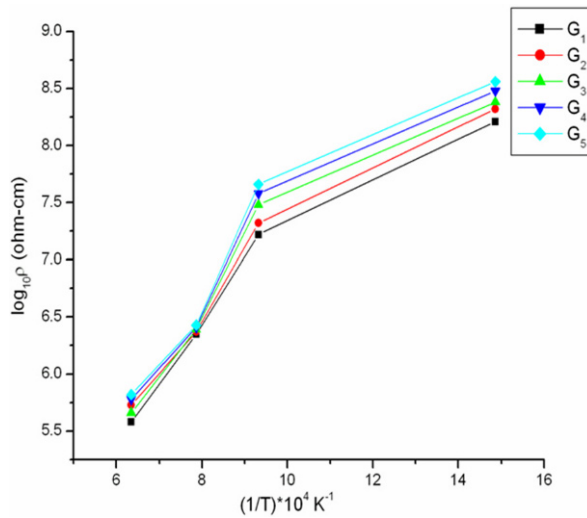


Fig. 3. Resistivity ($\log_{10} \rho$) versus $1/T \times 10^4$ graph of mullite precursor gels containing increasing concentration of nickel, sintered at 800 °C, 1000 °C and 1300 °C.

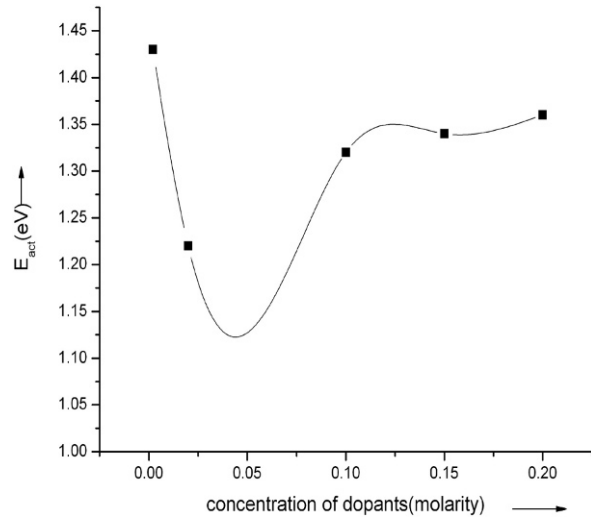


Fig. 5. Activation energy (E_g) vs concentration curve of mullite precursor gels containing increasing concentration of nickel, sintered at 800 °C, 1000 °C and 1300 °C.

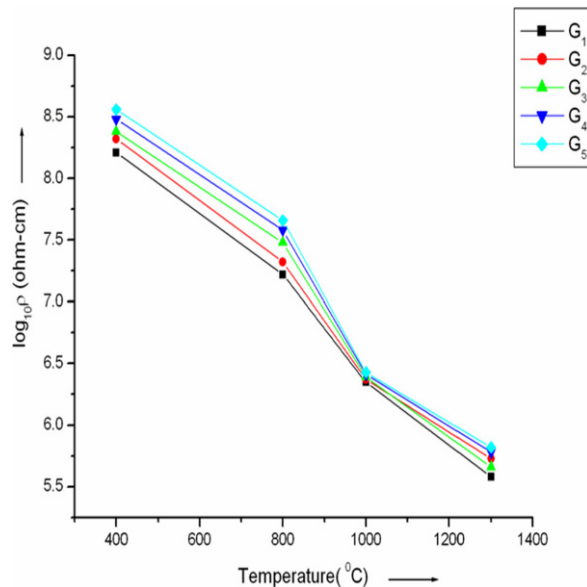


Fig. 4. Resistivity versus temperature (°C) of mullite precursor gels containing increasing concentration of nickel, sintered at 800 °C, 1000 °C and 1300 °C.

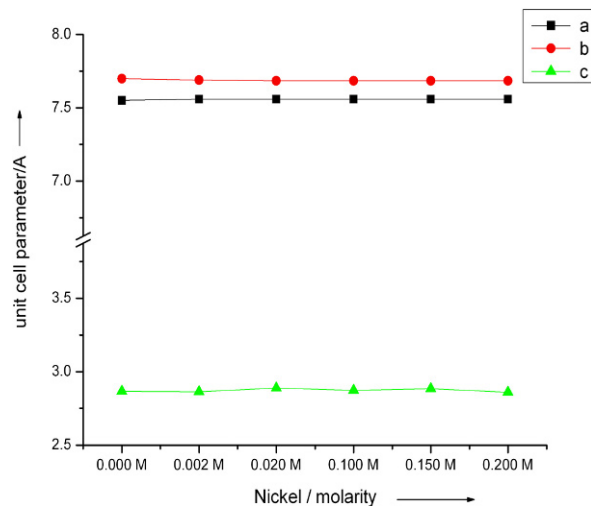


Fig. 6. Variation of unit cell parameters (a, b, c) with nickel molarity at 1300 °C.

From the E_{act} versus concentration curve, (Fig. 5), it can be inferred that E_{act} decreases with concentration and achieves its minimum value of 1.12 eV.

The substitution of Al^{3+} ion in the mullite lattice by Ni^{2+} ion disturbs the electro neutrality of

the composite. In the case of such substitution, Ni^{2+} forms acceptor centers in the Al sublattice. So, it leads to some decrease in the electron concentration in the case of the n -type semiconductor, or an increase in the electron hole concentration in the case of the p -type semiconductor. In Ni^{2+} doped mullite, the electrons which are released from the valence band jump into the donor level, and this is probably responsible for lowering the resistivity [25–27].

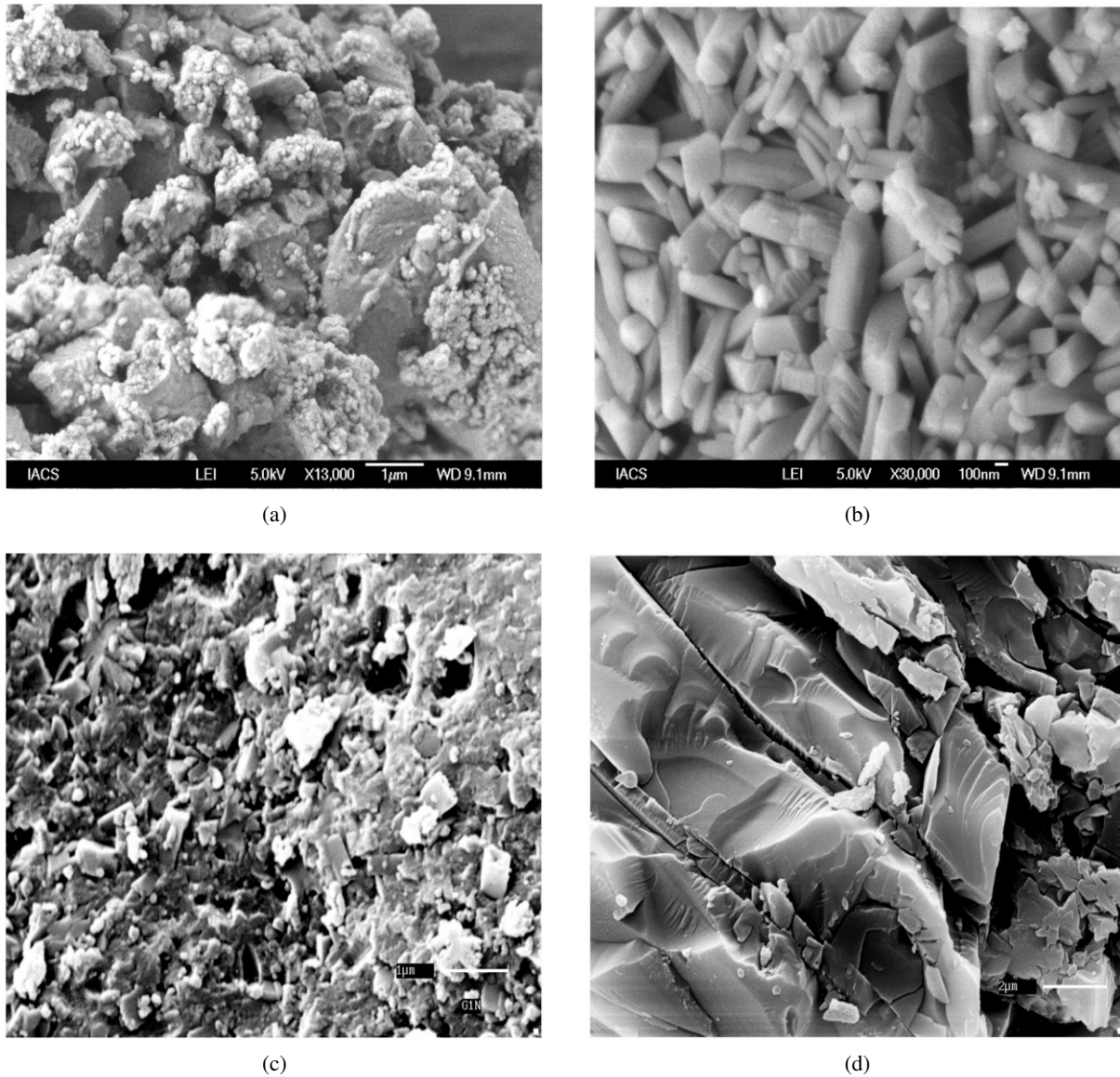


Fig. 7. FESEM of mullite precursor gels doped with nickel for G_1 and G_5 samples sintered at 1000 °C and 1300 °C: a) G_1 ; $T = 1000$ °C, b) G_5 ; $T = 1000$ °C, c) G_1 ; $T = 1300$ °C; d) G_5 ; $T = 1300$ °C.

There are two possible explanations of increasing E_{act} after attaining its minimum value at 0.15 M (Fig. 5): either complete incorporation of Ni^{2+} in the mullite structure or dissolution of Ni^{2+} ions in the Si-rich glassy phase. The dissolution of Ni^{2+} ions in the glassy phase should dominate over the incorporation of Ni^{2+} 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.

Mullite crystallizes in an orthorhombic system and its unit cell is characterized with three lattice parameters. The unit cell parameters variation with molarity of mullite is given in Fig. 6 for the 1300 °C sample. It has been observed that the dimension in a -axis of mullite does not change, in b -axis contracts, but in c -axis increases steadily for both gels sintered at 1300 °C. The observed changes are not necessarily caused by nickel entrance into mullite lattice and could be explained by the changeable ratio of

$\text{Al}_2\text{O}_3/\text{SiO}_2$ in the mullite lattice. The unit cell volume increases with increasing the concentration of nickel ions [30] (Fig. 6). It has been noticed that with the increase of doping level the mullite amount in the sample increases with the formation of nickel silicate and nickel aluminate. The very small change of the unit cell parameters at higher concentrations can be explained by nickel tendency to form a glass phase with SiO_2 and Al_2O_3 [31, 32]. As the excess of nickel does not form any stable crystal phase, we can assume formation of amorphous glassy phase. The morphology of mullite particles with the lowest (G_1) and the highest (G_5) concentrations of Ni^{2+} , sintered at 1000 °C and 1300 °C was investigated by FESEM. The micrograph for G_1 and G_5 shows acicular morphology of an average size of 200 nm at 1000 °C (see Fig. 7a,b) [13, 32, 33], and the micrograph for G_1 and G_5 at 1300 °C shows thick plate like morphology (see Fig. 7c,d) [13, 32–34]. The mullite content and crystallization degree in all the G_5 samples were greater than in G_1 composites, indicating the catalytic effect of the Ni^{2+} ions [17, 23].

4. Conclusions

Nickel doped mullite composites were synthesized by the sol-gel technique and their phase evolution, activation energy and unit cell parameter were investigated. The results showed that with an increase in Ni^{2+} concentration the crystallization of mullite was enhanced, which is evident from X-ray diffraction and FESEM of the composites. The activation energy of resistivity, E_{act} , attains a minimum value of 1.22 eV at 0.02 M. It has been observed that the activation energy of resistivity, E_{act} corresponds to semiconductors.

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