

## Effect of Ce<sup>4+</sup> substitution on the structural, electrical and dielectric properties of NiAl<sub>2</sub>O<sub>4</sub> spinel

C. O. Augustin<sup>\*1</sup>, K. Hema<sup>2</sup>, L. John Berchmans<sup>1</sup>, R. Kalai Selvan<sup>1</sup>, and R. Saraswathi<sup>2</sup>

<sup>1</sup> Central Electrochemical Research Institute, Karaikudi – 630 006, India

<sup>2</sup> Department of Materials Science, Madurai Kamaraj University, Madurai – 625 021, India

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The structural, electrical and dielectric properties of a series of Ni<sub>1-x</sub>Ce<sub>x</sub>Al<sub>2</sub>O<sub>4</sub> ( $x = 0.0, 0.2, 0.4, 0.6, 0.8$ ) compositions have been studied. The samples were prepared by a novel glycine–nitrate combustion synthesis route. The substitution of Ce<sup>4+</sup> for Ni<sup>2+</sup> results in an increase in the lattice constant owing to the larger size of the substituent. The X-ray density increases with increasing Ce<sup>4+</sup> content. The IR spectra show two fundamental absorption bands, which are shifted gradually towards higher energy with the addition of Ce<sup>4+</sup>. The UV–visible spectra confirm the preference of Ni<sup>2+</sup> for the octahedral site. The dc electrical conductivity increases with increasing temperature due to the mobility of thermally activated charge carriers. Due to the electrostatic screening effect of B-site cations, the conductivity decreases with increasing Ce<sup>4+</sup> content. The dielectric constant and loss tangent of the synthesized compounds show the normal behavior of spinel compounds. The ac electrical conductivity increases with increasing applied frequency and decreases with increasing Ce<sup>4+</sup> substitution.

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### 1 Introduction

Metal aluminates, MAl<sub>2</sub>O<sub>4</sub> (M = Ni, Co, Zn, Mg, Ca, Sr), are a cohesive class of materials, which have potential applications in various fields due to their immobilized characteristics. They are used as catalysts [1], refractories [2], pigments [3], proton conductors [4], anodes for SOFCs [5] and luminescent materials [6]. The overall physicochemical properties of spinels mainly depend upon the cation distribution among the tetrahedral and octahedral sites in the crystal lattice. The cation distribution in spinels is represented by the formula (A<sub>1-x</sub>B<sub>x</sub>)<sub>T</sub>[A<sub>x</sub>B<sub>2-x</sub>]<sub>O</sub>O<sub>4</sub>, where  $x$  is the inversion parameter, which mainly depends upon the temperature. At lower temperatures NiAl<sub>2</sub>O<sub>4</sub> has an almost inverse spinel structure ( $x \geq 2/3$ ) and at higher temperature the cations are distributed randomly ( $x = 2/3$ ), leading to the inversion [7, 8]. The most important applications of NiAl<sub>2</sub>O<sub>4</sub> materials are as good electrocatalysts for the oxidation of organic compounds and nitrous oxide [9], and also as inert anodes in aluminum electrolysis [10].

NiAl<sub>2</sub>O<sub>4</sub> and substituted compounds have been prepared by various methods such as solid-state fusion [11], the sol–gel method [12], microwave solid-state sintering [13], the sonochemical method [14], co-precipitation [15], etc. To our knowledge no studies have been reported on the preparation of Ce<sup>4+</sup>-substituted NiAl<sub>2</sub>O<sub>4</sub> compounds by the combustion method for their use as electrode materials for high-temperature electrochemical applications. Combustion synthesis is a well-known technique to produce well-dispersed nanocrystalline compounds with a uniform particle size distribution [16]. The aim of the present study was to synthesize nanocrystalline NiAl<sub>2</sub>O<sub>4</sub> by a combustion method and to investigate

<sup>\*</sup> Corresponding author: e-mail: caugustin@rediffmail.com, Fax: +91 4565 227713, +91 4565 227779

the effect of  $\text{Ce}^{4+}$  substitution on its structural, electrical and dielectric properties using X-ray diffraction (XRD), Fourier transform IR (FTIR), UV–visible, dc conductivity and ac conductivity methods.

## 2 Experimental

Nanocrystalline  $\text{Ni}_{1-x}\text{Ce}_x\text{Al}_2\text{O}_4$  ( $x = 0.0, 0.2, 0.4, 0.6, 0.8$ ) compositions were synthesized by a novel glycine–nitrate combustion synthesis process. The starting materials were  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CeO}_2$ ,  $\text{HNO}_3$ ,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{CH}_2\text{NH}_2\text{COOH}$ . The metal nitrate salts act as cation precursors and glycine as a fuel. The experimental details are given elsewhere [17].

The structural homogeneity, crystal structure, phase formation and crystalline size were determined from XRD patterns using  $\text{CuK}\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation with  $2\theta$  values ranging from  $10^\circ$  to  $80^\circ$  using a JEOL 8030 X-ray diffractometer. The nanocrystalline nature of the synthesized compounds was determined using the Debye–Scherrer formula ( $0.9\lambda/\beta \cos \theta$ , where  $\lambda$  is the wavelength of the target and  $\beta$  is the full width at half maximum of diffracted (311) plane). The X-ray density was calculated using the formula  $D_{\text{hkl}} = 8M/Na^3$ , where  $M$  is the molecular weight of the sample,  $N$  is the Avogadro number and  $a$  is the lattice parameter of the sample. The FTIR spectra of the samples were recorded in KBr discs in the range  $400\text{--}1000 \text{ cm}^{-1}$  using a Paragon-500, Perkin Elmer FTIR spectrophotometer.

The dc electrical conductivity was recorded as a function of temperature using a modified four-probe setup to study the effect of substitution with  $\text{Ce}^{4+}$ . The frequency variations of ac conductivity were measured at room temperature from 100 Hz to 10 kHz using a computerized LCRTZ test system (VLCRTZIP). For good ohmic contact for these measurements, silver paste was applied on both surfaces of the sample pellets before being sandwiched between the two electrodes of the sample holder.

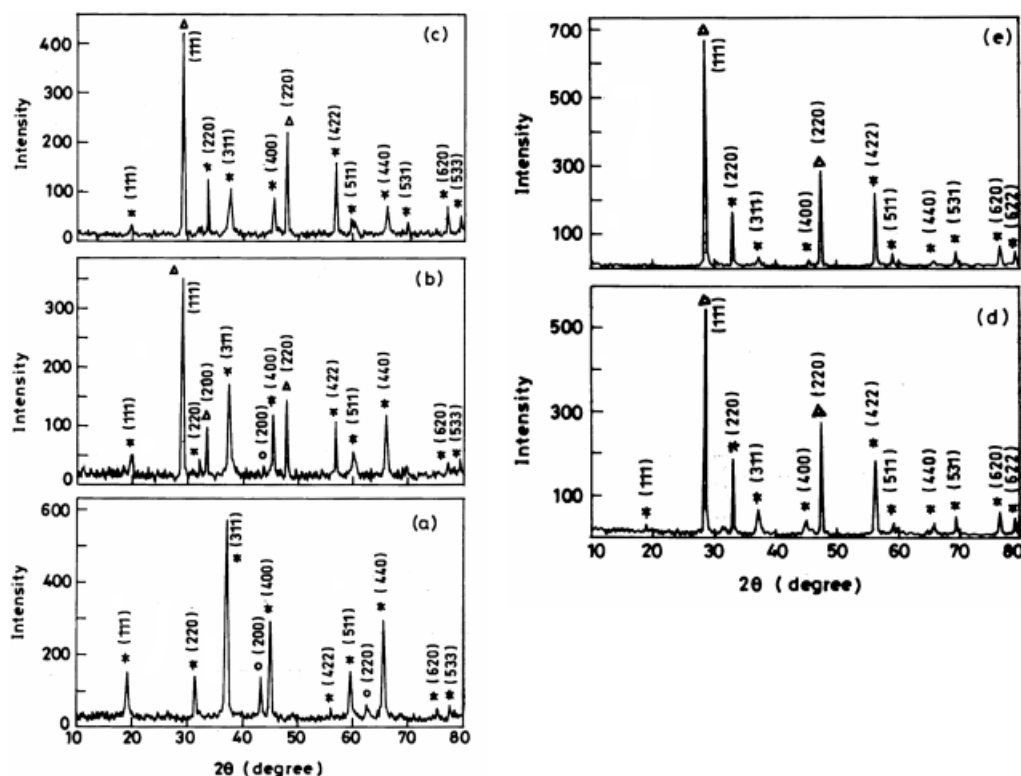
## 3 Results and discussion

### 3.1 X-ray diffraction

The structural identification and changes in crystallinity were studied using XRD. The XRD patterns of  $\text{NiAl}_2\text{O}_4$  with different molar substitutions of  $\text{Ce}^{4+}$  are shown in Fig. 1. It is seen that all the samples were polycrystalline with a cubic spinel structure. Figure 1a shows the XRD pattern of  $\text{NiAl}_2\text{O}_4$  with well-defined and high-intensity peaks, matching standard data except in the case of two minor peaks (200) and (220), corresponding to NiO. Figures 1b–e show the patterns for  $\text{Ce}^{4+}$ -substituted  $\text{NiAl}_2\text{O}_4$ . A notable feature in the patterns is that with increasing substitution, the intensities of  $\text{NiAl}_2\text{O}_4$  peaks (311) and (440) are found to decrease continuously. At the same time a new sharp peak (111) corresponding to  $\text{CeO}_2$  is seen to appear, whose intensity increases continuously up to the maximum substitution. Values of the lattice constants and structural parameters are given in Table 1. The lattice constant values increase with increasing substitution, due to the difference in ionic radii between  $\text{Ni}^{2+}$  and  $\text{Ce}^{4+}$ , and are in fairly good agreement with reported values [18].

The X-ray intensities of (422), (220), (440) and (511) planes are more sensitive to cations in tetrahedral and octahedral sites, and oxygen ion parameter [19, 20]. It is reported that  $\text{Ni}^{2+}$  has a strong preference for B-sites due to the inverse spinel nature leading to the following cation distribution:  $(\text{Al})_{\text{T}}[\text{NiAl}]_{\text{O}}\text{O}_4$ . Table 1 shows that increasing the concentration of  $\text{Ce}^{4+}$  increases the intensity of the (422) peak,  $I_{422}$ , which suggests that  $\text{Ce}^{4+}$  has a preference for occupying the tetrahedral site [21]. At the same time the intensity of the (440) peak,  $I_{440}$ , decreases with increasing substitution, which could be attributed to the replacement of  $\text{Ni}^{2+}$  by  $\text{Ce}^{4+}$ . Altogether it is observed that the substitution of  $\text{Ni}^{2+}$  (B-sites) with  $\text{Ce}^{4+}$  takes place at the A-site instead of at the B-site due to the strong preference of  $\text{Ce}^{4+}$  for the A-site. The crystalline size was found to vary between 25 and 43 nm over the range of  $\text{Ce}^{4+}$  substitution investigated. It is evident from Table 1 that the X-ray density tends to increase with increasing concentration of  $\text{Ce}^{4+}$ .

From a study of the phases [17], it was found that the sample sintered at  $1000^\circ\text{C}$  contained 82%  $\text{NiAl}_2\text{O}_4$  in comparison to the reported value of 50%  $\text{NiAl}_2\text{O}_4$  at  $1200^\circ\text{C}$  synthesized by the conventional solid-state reaction [13]. This demonstrates the superiority of the glycine–nitrate combustion process for the synthesis of new materials.



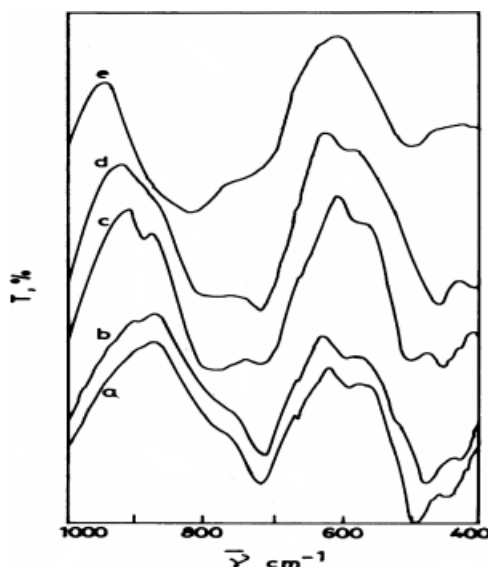
**Fig. 1** XRD patterns of  $\text{Ni}_{1-x}\text{Ce}_x\text{Al}_2\text{O}_4$ : a)  $x = 0.0$ , b)  $x = 0.2$ , c)  $x = 0.4$ , d)  $x = 0.6$ , e)  $x = 0.8$ , \*,  $\text{NiAl}_2\text{O}_4$ ; ○,  $\text{NiO}$ ; Δ,  $\text{CeO}_2$ .

### 3.2 FTIR spectroscopy

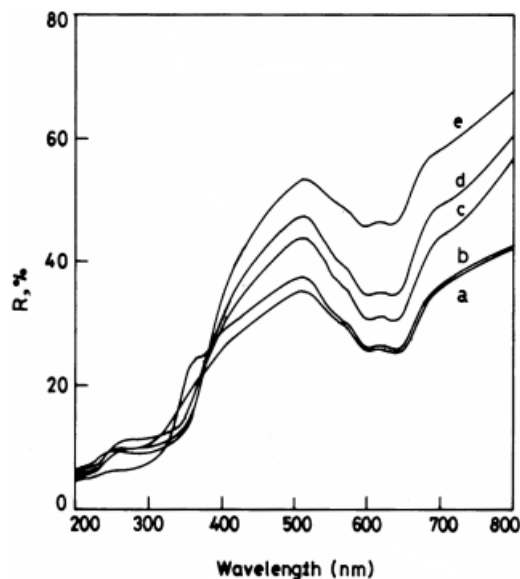
FTIR spectra of the combustion-synthesized  $\text{Ni}_{1-x}\text{Ce}_x\text{Al}_2\text{O}_4$  ( $x = 0.0, 0.2, 0.4, 0.6, 0.8$ ) were recorded between 400 and 1000  $\text{cm}^{-1}$  at room temperature, and are shown in Fig. 2. The spectra show the position of the cations in the crystal structure with oxygen ions and their vibration modes. The spectrum of non-substituted  $\text{NiAl}_2\text{O}_4$  shows three absorption bands at 721, 602 and 494  $\text{cm}^{-1}$ . The band at 721  $\text{cm}^{-1}$  can be attributed to the tetrahedrally coordinated Al–O bond. The band at 602  $\text{cm}^{-1}$  may be due to the stretching vibration of Al–O for octahedrally coordinated aluminum ions [22]. The band at 494  $\text{cm}^{-1}$  is attributed to the octahedrally coordinated Ni–O bands. The three bands confirm the formation of  $\text{NiAl}_2\text{O}_4$  with inverse spinel structure. The FTIR spectra of the substituted compounds show peak shifts due to the presence of  $\text{Ce}^{4+}$ . The high-frequency band  $\nu_1$  varies in the range 722.13–803.43  $\text{cm}^{-1}$  and the low-frequency band  $\nu_2$  varies in the range 494–506  $\text{cm}^{-1}$ . The difference in the band positions is expected because of the

**Table 1** XRD parameters of  $\text{Ce}^{4+}$ -substituted  $\text{NiAl}_2\text{O}_4$ .

| $\text{Ni}_{1-x}\text{Ce}_x\text{Al}_2\text{O}_4$ | $a$ (nm) | crystalline size (nm) | X-ray density ( $\text{g}/\text{cm}^3$ ) | $I_{422}$ | $I_{440}$ |
|---------------------------------------------------|----------|-----------------------|------------------------------------------|-----------|-----------|
| $x = 0.0$                                         | 8.017    | 48.5                  | 4.54                                     | 2.84      | 50.85     |
| $x = 0.2$                                         | 8.043    | 36.3                  | 4.92                                     | 27.16     | 30.18     |
| $x = 0.4$                                         | 8.092    | 29.3                  | 5.24                                     | 31.25     | 13.15     |
| $x = 0.6$                                         | 8.095    | 36                    | 5.76                                     | 32.16     | 04.05     |
| $x = 0.8$                                         | 8.107    | 24                    | 6.25                                     | 35.45     | 01.36     |



**Fig. 2** FTIR spectra of Ni<sub>1-x</sub>Ce<sub>x</sub>Al<sub>2</sub>O<sub>4</sub>: (a)  $x = 0.0$ , (b)  $x = 0.2$ , (c)  $x = 0.4$ , (d)  $x = 0.6$ , (e)  $x = 0.8$ .



**Fig. 3** UV-visible spectra of Ni<sub>1-x</sub>Ce<sub>x</sub>Al<sub>2</sub>O<sub>4</sub>: (a)  $x = 0.0$ , (b)  $x = 0.2$ , (c)  $x = 0.4$ , (d)  $x = 0.6$ , (e)  $x = 0.8$ .

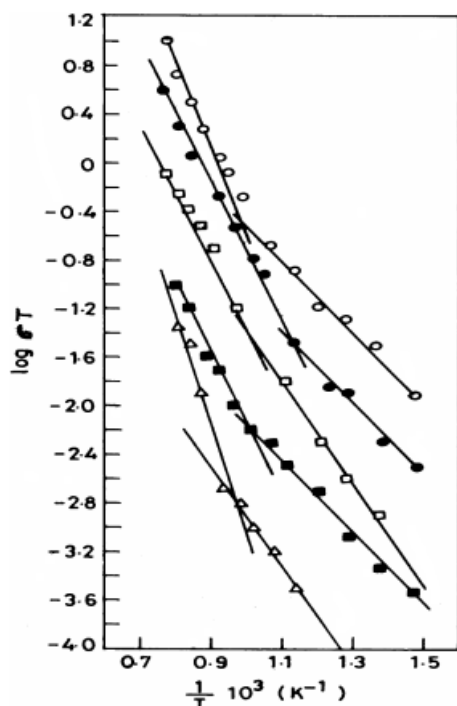
difference in the Al<sup>3+</sup>–O<sup>2-</sup> distances for tetrahedral and octahedral sites. It is observed that with increasing concentration of Ce<sup>4+</sup> ( $x \geq 0.4$ ) the absorption peak around 700 cm<sup>-1</sup> is found to broaden due to structural changes in the aluminate compound.

### 3.3 UV-visible spectroscopy

The diffuse reflectance spectra of Ce<sup>4+</sup>-substituted NiAl<sub>2</sub>O<sub>4</sub> are shown in Fig. 3. The non-substituted NiAl<sub>2</sub>O<sub>4</sub> shows absorption bands at around 360 and 700 nm, and a shoulder at 510 nm. These spectra also confirm the inverse spinel structure, i.e. the Ni<sup>2+</sup> ions are situated in the octahedral sites as may be inferred from the absorption bands at ~700 and 360 nm [23]. As the Ce<sup>4+</sup> substitution increases, the absorption band at 360 nm decreases and a small absorption band at 610 nm appears, which may be due to preferential occupation of the tetrahedral site.

### 3.4 Dc electrical conductivity

The temperature dependence of the dc electrical conductivity of Ni<sub>1-x</sub>Ce<sub>x</sub>Al<sub>2</sub>O<sub>4</sub> shows that the conductivity increases with increasing temperature. This behavior is similar to that observed for semiconductors. It is noticed that pure NiAl<sub>2</sub>O<sub>4</sub> has a conductivity of  $1.19 \times 10^{-3}$  S cm<sup>-1</sup> at 400 °C, increasing to  $7.77 \times 10^{-3}$  S cm<sup>-1</sup> at 1000 °C. The increase in dc conductivity with temperature is due to the increase in thermally activated drift mobility of the charge carriers as well as to increased migration of metallic ions [24]. At lower temperatures the conductivity mainly depends upon electronic conduction and at higher temperatures both electrons and polarons take part in the conduction process. In general, the electrical conductivity of the samples is mainly contributed to by the reaction  $\text{Ni}^{2+} \rightleftharpoons \text{Ni}^{3+} + \text{e}^-$  at the B-site. It is also observed that conductivity decreases with increasing Ce<sup>4+</sup> substitution. From structural studies it has been confirmed that Ni<sup>2+</sup> occupy B-sites, Ce<sup>4+</sup> A-sites, and Al<sup>3+</sup> both A- and B-sites, due to the inverse spinel structure. Ni<sup>2+</sup> ions are replaced by Ce<sup>4+</sup> ions, which migrate from B-sites to A-sites. Therefore, the B-site active cation concentration of Ni<sup>2+</sup> decreases, which leads to a decrease in conductivity [25, 26]. Table 1 shows a decrease in crystalline size with increasing substitution. If the grain size decreases, the grain boundary



**Fig. 4** Arrhenius plots for  $\text{Ni}_{1-x}\text{Ce}_x\text{Al}_2\text{O}_4$ : ( $\circ$ )  $x = 0.0$ , ( $\bullet$ )  $x = 0.2$ , ( $\square$ )  $x = 0.4$ , ( $\blacksquare$ )  $x = 0.6$ , ( $\triangle$ )  $x = 0.8$ .

volume increases leading to disorder and crystal imperfections. Due to the size effect, the crystalline size is smaller than the electron mean free path, and grain boundary scattering dominates, decreasing the electrical conductivity [27].

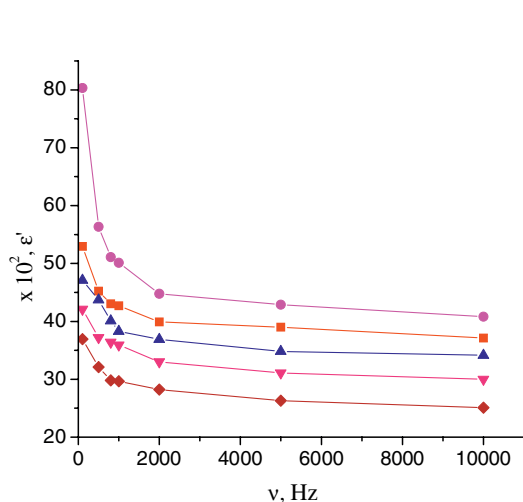
Activation energies were calculated from Arrhenius plots (Fig. 4) using the equation  $\sigma T = \sigma_0 \exp(-E_a/kT)$  and they are given in Table 2. Here,  $\sigma_0$  is the pre-exponential factor,  $E_a$  is the activation energy for dc conductivity and  $k$  is the Boltzmann constant. The activation energies for the non-substituted  $\text{NiAl}_2\text{O}_4$  are 0.57 and 0.97 eV. As the  $\text{Cr}^{4+}$  substitution increases, the activation energy increases, decreasing the conduction due to grain boundary effect [28].

### 3.5 Ac electrical properties

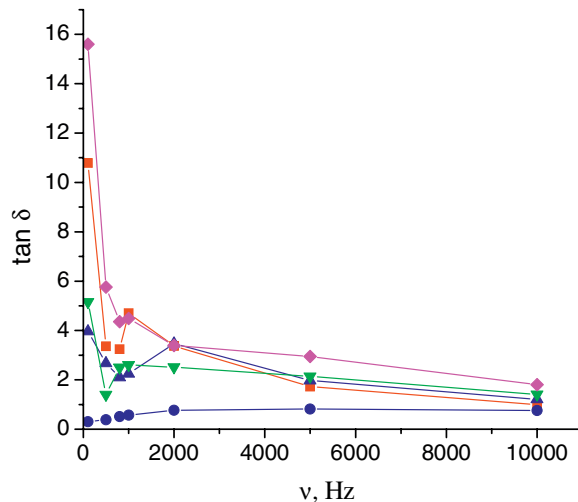
The dielectric property of a material depends upon the method of preparation, chemical composition, grain size, calcination temperature and applied frequency. The individual high-conductivity grains are produced under the calcination temperature and separated by low-conductivity grain boundaries, which behave as inhomogeneous dielectric materials. Figure 5 shows the variation of dielectric constant with frequency from 100 Hz to 10 kHz for the compounds measured at room temperature. It shows a normal dielectric behavior, similar to semiconductors (decrease in dielectric constant with increasing frequency, which is due to the Maxwell interfacial polarization) [29]. According to the Maxwell–Wagner model, the dielectric structure of a spinel material consists of a conducting layer of large grains and grain boundaries of lower conductivity. Such a bi-layer results from high-temperature sintering. The decrease in dielectric constant with increasing frequency is due to the fact that the electronic exchange between  $\text{Ni}^{2+}$  and  $\text{Ni}^{3+}$  ions cannot follow the external applied frequency. Figure 5 also shows the variation of dielectric constant with increasing  $\text{Ce}^{4+}$  content. As the  $\text{Ce}^{4+}$  concentration increases the value of the dielectric constant decreases. This variation mainly depends upon the number of space charge carriers and the resistivity of the samples arising from the inhomogeneous dielectric structure. From the XRD observations it is clear that the B-site cations  $\text{Ni}^{2+}/\text{Ni}^{3+}$  decrease with increasing  $\text{Ce}^{4+}$  content. Hence, the effect of electric polarization is reduced because of the unavailability of the B-site cations. Metal ions with different valence states occupying the same site lead to the polarization phenomenon, which explains the decrease in dielectric constant with increasing  $\text{Ce}^{4+}$  content [30].

**Table 2** Activation energy values of  $\text{Ce}^{4+}$ -substituted  $\text{NiAl}_2\text{O}_4$ .

| activation energy (eV) | $x = 0.0$ | $x = 0.2$ | $x = 0.4$ | $x = 0.6$ | $x = 0.8$ |
|------------------------|-----------|-----------|-----------|-----------|-----------|
| region I               | 0.5746    | 0.8426    | 0.6465    | 0.6274    | 0.8045    |
| region II              | 0.9717    | 1.2642    | 0.9960    | 2.4136    | 1.5516    |



**Fig. 5** (online colour at: [www.pss-a.com](http://www.pss-a.com)) Dielectric constant vs. frequency for  $\text{Ni}_{1-x}\text{Ce}_x\text{Al}_2\text{O}_4$ : (■)  $x = 0.0$ , (●)  $x = 0.2$ , (▲)  $x = 0.4$ , (▼)  $x = 0.6$ , (◆)  $x = 0.8$ .



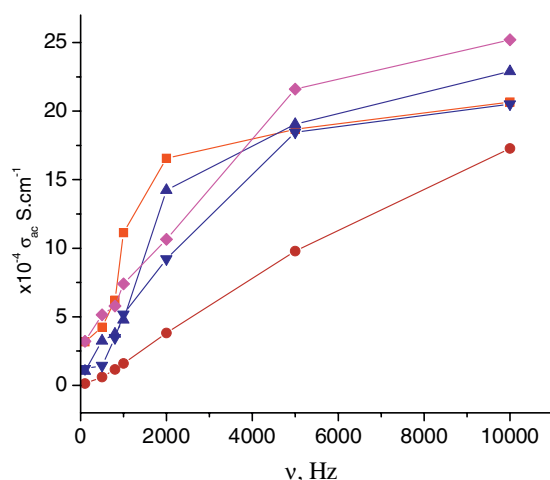
**Fig. 6** (online colour at: [www.pss-a.com](http://www.pss-a.com)) Dielectric loss tangent vs. frequency for  $\text{Ni}_{1-x}\text{Ce}_x\text{Al}_2\text{O}_4$ : (■)  $x = 0.0$ , (●)  $x = 0.2$ , (▲)  $x = 0.4$ , (▼)  $x = 0.6$ , (◆)  $x = 0.8$ .

Figure 6 shows the variation of loss tangent ( $\tan \delta$ ) with frequency for all the samples measured at room temperature. At low frequencies the loss tangent is very high, while at high frequencies it is very low. At low frequencies the energy requirements for the electrical exchange  $\text{Ni}^{2+} \leftrightarrow \text{Ni}^{3+} + e^-$  are large. Hence the loss tangent is very high. However, at high frequencies a lower energy is enough to maintain the changes and, hence, the loss tangent is low. This mechanism can be correlated with the Koop bi-layer formation at lower frequencies at which the grain boundary effect is predominant. Therefore the resistivity of the material is high. However, in the higher frequency region the grain effect is large, and the conduction is a maximum [31].

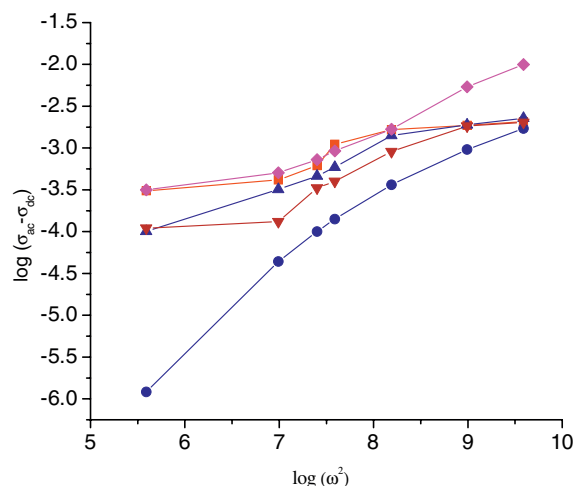
Figure 6 also shows the effect of  $\text{Ce}^{4+}$  substitution on the loss tangent. The loss tangent increases with increasing  $\text{Ce}^{4+}$  content. This is due to an increase in resistivity due to the conduction mechanism. The composition dependence of this behavior is similar to that of the dielectric constant mechanism. The dielectric relaxation peaks are observed at 1.0 kHz for  $x = 0.0, 0.4, 0.8$  and at 500 Hz for  $x = 0.2$ . This occurs when the jumping frequency of localized charge carriers approximately equals that of the externally applied ac electric field. The appearance of dielectric relaxation peaks could be related to the collective contribution of both types of charge carriers, which could be explained by the Rezlescu model [32].

Figure 7 shows the dependence of ac electrical conductivity,  $\sigma_{ac}$ , on frequency. It can be seen that the ac conductivity increases with increasing frequency. The electrical conduction of spinels is explained by a hopping mechanism involving the charge carriers at the B-site. The applied ac frequency of the sample enhances the hopping frequency as well as the mobility of the charge carriers, which results in an increase in conductivity. It can also be seen that the ac conductivity decreases with increasing concentration of  $\text{Ce}^{4+}$  ions due to the grain boundary effect.

Figure 8 shows the relationship between  $\log(\sigma_{ac} - \sigma_{dc})$  and  $\log(\omega^2)$ . It can be seen that the plots are straight lines in accordance with the equation of [33]:  $(\sigma_{ac} - \sigma_{dc}) = \omega^2 \tau / (1 + \omega^2 \tau^2)$ . At the applied frequency  $\omega < 10^9$  Hz,  $\tau$  is very small ( $\approx 10^{-10}$  s). Therefore  $\omega^2 \tau^2$  becomes  $\ll 1$ , which can be neglected, reducing the equation to  $(\sigma_{ac} - \sigma_{dc}) = \omega^2$ . In such a case a plot of  $\log(\sigma_{ac} - \sigma_{dc})$  vs.  $\log(\omega^2)$  should be a straight line, as seen in Fig. 8. Hence, it can be construed that the increase in ac conductivity with increasing frequency is due to conduction by small polaron hopping.



**Fig. 7** (online colour at: www.pss-a.com) Ac conductivity vs. frequency for  $\text{Ni}_{1-x}\text{Ce}_x\text{Al}_2\text{O}_4$ : (■)  $x = 0.0$ , (●)  $x = 0.2$ , (▲)  $x = 0.4$ , (▼)  $x = 0.6$ , (◆)  $x = 0.8$ .



**Fig. 8** (online colour at: www.pss-a.com)  $\log(\sigma_{ac} - \sigma_{dc})$  vs.  $\log(\omega^2)$  for  $\text{Ni}_{1-x}\text{Ce}_x\text{Al}_2\text{O}_4$ : (■)  $x = 0.0$ , (●)  $x = 0.2$ , (▲)  $x = 0.4$ , (▼)  $x = 0.6$ , (◆)  $x = 0.8$ .

## 4 Conclusion

$\text{Ce}^{4+}$ -substituted nanocrystalline  $\text{NiAl}_2\text{O}_4$  was successfully synthesized by a novel glycine–nitrate combustion method. X-ray studies confirm the cubic nature of the synthesized compounds with  $\text{Ce}^{4+}$  ions in the tetrahedral site,  $\text{Ni}^{2+}$  ions in the octahedral site and  $\text{Al}^{3+}$  ions in both tetrahedral and octahedral sites. FTIR and UV–visible studies show that the compounds have an inverse spinel structure. It is found that the dc electrical conductivity of the compounds increases with increasing temperature due to an increase in the mobility of the thermal carriers. It is also observed that the conductivity decreases with increasing  $\text{Ce}^{4+}$  substitution due to the blocking nature of rare earth ions. The ac conductivity increases with increasing frequency due to hopping of polarons and decreases with increasing  $\text{Ce}^{4+}$  substitution.

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