



# Effect of rare earth yttrium substitution on the structural, dielectric and electrical properties of nanosized nickel aluminate



Rohan Samkaria, Vimal Sharma\*

Department of Physics, National Institute of Technology Hamirpur, 177005, India

## ARTICLE INFO

### Article history:

Received 5 March 2013

Received in revised form 13 August 2013

Accepted 29 August 2013

Available online 9 September 2013

### Keywords:

Spinel oxides

Nanocrystalline

X-ray diffraction

Dielectric constant

AC conductivity

DC resistivity

## ABSTRACT

In this communication, we have systematically investigated the effect of yttrium substitution on the structural, dielectric and electrical properties of nanosized  $\text{NiAl}_{2-2x}\text{Y}_{2x}\text{O}_4$  series (where  $x = 0.00, 0.01, 0.02, 0.03, 0.04, 0.05, 0.07$  and  $0.10$ ). All the samples were prepared by chemical coprecipitation method. Powder X-ray diffraction (XRD) confirmed the formation of single phase cubic spinel structure in all the samples. Replacement of  $\text{Al}^{3+}$  ions by  $\text{Y}^{3+}$  ions results in a slight increase of lattice parameter. It was inferred that the substitution of yttrium suppressed the crystallite size growth. Transmission electron microscopy (TEM) validated the nanocrystalline nature of the samples. The Fourier transform infrared spectroscopy (FTIR) confirmed the preference of  $\text{Y}^{3+}$  ions at the octahedral B site. Room temperature dielectric properties, namely dielectric constant ( $\epsilon'$ ), dielectric loss ( $\tan \delta$ ), ac conductivity ( $\sigma_{a.c.}$ ) and electrical modulus ( $M''$ ) were studied as a function of applied frequency in the range from 1 kHz to 1 MHz. These studies indicate that all the samples show usual dielectric dispersion which is due to Maxwell–Wagner type Interfacial Polarization. The ac conductivity measurement suggests that the conduction mechanism is due to small polaron hopping. The electrical modulus results clearly indicate the presence of non-Debye type of dielectric relaxation in all the samples. The dc electrical resistivity measured in the temperature range of 303–373 K was found to increase with temperature and yttrium content.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Spinel oxides having general formula  $\text{AB}_2\text{O}_4$ , where A and B are the divalent and trivalent cations respectively, are of particular interest due to their structural features. They provide variety of interesting magnetic, electrical and optical properties [1]. Among these materials aluminum based nickel aluminate ( $\text{NiAl}_2\text{O}_4$ ) spinel has received great deal of attention as a technologically important material on account of its attractive properties such as high melting point and large surface area. Therefore it has been extensively used as a component material in high temperature fuel cells and for catalytic purposes [2,3].

The main focus of current research activities on spinel aluminates is two-fold, viz.: improvement of properties by reducing the dimensions down to nanoscale and to study the doping effects of various ions on the structural, dielectric and electrical properties [4–8]. An understanding of the dielectric properties in terms of temperature and frequency of the applied field was investigated by Kurien et al. [9]. The literature survey shows that no attempt has been made toward the study of doping effects on the structural

and electrical transport properties of nanosized  $\text{NiAl}_2\text{O}_4$ . However, earlier studies have shown that  $\text{Y}^{3+}$  substituted nanosized Ni ferrites are excellent candidates for high frequency applications due to their high resistivity and low dielectric loss [10,11], owing to analogy between the polarization and conduction mechanism in spinel ferrites and aluminates. A rich behavior can also be evolved in the electrical transport properties of nanosized spinel aluminates with rare earth substitution at the octahedral B site. Therefore it is in this context that a detailed investigation on the structural and electrical transport properties of a nano  $\text{NiAl}_{2-2x}\text{Y}_{2x}\text{O}_4$  series assumes significance.

The chemical coprecipitation technique was used for the preparation of samples. This method yields a uniform crystallite size distribution and better control over the chemical composition of prepared samples when prepared in more basic conditions [12]. In the present study single phase compositions of  $\text{NiAl}_{2-2x}\text{Y}_{2x}\text{O}_4$  ( $x = 0.00$ – $0.10$ ) has been prepared, and the structural and electrical properties have been investigated systematically.

## 2. Experimental

All the compositions of nanocrystalline  $\text{NiAl}_{2-2x}\text{Y}_{2x}\text{O}_4$  system were prepared from Merck Germany GR grade chemicals viz.

\* Corresponding author. Tel.: +91 9459275085; fax: +91 1972 223834.

E-mail addresses: [rohan.samkaria@gmail.com](mailto:rohan.samkaria@gmail.com) (R. Samkaria), [vml16sharma@yahoo.co.in](mailto:vml16sharma@yahoo.co.in) (V. Sharma).

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Y}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and aqueous  $\text{NH}_3$  (Merck India, 30%).

The samples were prepared using stoichiometric quantities of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (5.816 g) and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (15.005 g) then dissolving them separately in 100 mL deionized water and adding simultaneously into a flask containing 200 mL deionized water. Ammonia solution was added drop wise till the pH value 10 was attained. The solution was continuously stirred by a magnetic stirrer for 1 h and aged at room temperature overnight. The precipitates were filtered and washed with deionized water and then dried at  $120^\circ\text{C}$  for 16 h in a hot air oven. The dried samples were calcined at  $950^\circ\text{C}$  in air in a tube furnace programmed at a fixed heating rate of  $5^\circ\text{C}/\text{min}$  for 8 h. The yttrium doped derivatives of  $\text{NiAl}_{2-2x}\text{Y}_{2x}\text{O}_4$  system were also prepared by adding the appropriate stoichiometric quantities of dopant salt  $\text{Y}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and following the same procedure as stated above.

The X-ray diffraction pattern of the powder samples were recorded with a Panalytical 3050/60 Xpert-PRO using  $\text{Cu K}\alpha$  radiation. The FTIR spectrum was recorded in the IR region from 400 to  $4000\text{ cm}^{-1}$  by Perkin Elmer Spectrum-65. Particle sizes were analyzed by means of Transmission electron microscope JEOL JEM 2100F operated at 200 kV. Room temperature dielectric properties were studied over the frequency range from 1 kHz to 1 MHz by using Wayne Kerr 6500B Impedance Analyzer. Measurements were accomplished with silver electrodes on the nanoparticle powder consolidated in the form of pellets of 13 mm diameter and thickness of 1 mm. The dc electrical resistivity was measured using Electrometer (Keithley, Model 6517A) in the temperature range of 303–373 K by two probe method.

### 3. Results and discussion

#### 3.1. Structural properties

X-ray diffraction patterns of  $\text{NiAl}_{2-2x}\text{Y}_{2x}\text{O}_4$  ( $x = 0.00, 0.01, 0.02, 0.03, 0.04, 0.05, 0.07$  and  $0.10$ ) system are shown in Fig. 1. All the samples show diffraction peaks with Miller indices (1 1 1), (2 2 0), (3 1 1), (4 0 0), (5 1 1) and (4 4 0) corresponding to the spinel structure of  $\text{NiAl}_2\text{O}_4$  (JCPDS Card No. 78-0552). Absence of any extra peak in all the samples indicates the formation of single phase spinel with cubic structure. However with the addition of yttrium the intensity of the peaks in XRD pattern is suppressed which indicates

that the system is going into a more disordered state. The lattice parameter ( $a$ ) was determined from the most intense peak (3 1 1) using the relation [13]:

$$a = d[(h^2 + k^2 + l^2)]^{1/2}, \quad (1)$$

where  $h, k$  and  $l$  are the miller indices;  $d$  is the value of interplanar spacing in XRD pattern. The unit cell volume was calculated using  $V_{\text{cell}} = a^3$ . The crystallite size ( $D$ ) was calculated from the line broadening of higher angle peak (4 4 0) using Scherrer formula [13]:

$$D = \frac{k\lambda}{\beta \cos \theta}, \quad (2)$$

where  $\beta$  is the full width at half maximum of the peak after correcting for peak broadening caused by the diffractometer,  $\lambda$  is the X-ray wavelength ( $1.5418 \text{ \AA}$ ),  $\theta$  the Bragg's angle and  $k$  a constant which is equal to 0.9 (for cubic system). The X-ray densities ( $d_{\text{X-ray}}$ ) of all the samples were calculated from the volume of a single unit cell using the relation [13]:

$$d_{\text{X-ray}} = \frac{ZM}{V_{\text{cell}}N_A}, \quad (3)$$

where  $Z$  is the number of formula units per unit cell ( $Z = 8$  for cubic spinel),  $M$  the molar mass,  $V_{\text{cell}}$  volume of the unit cell and  $N_A$  is the Avogadro's number.

Calculated values of lattice parameter ( $a$ ) and X-ray density ( $d_{\text{X-ray}}$ ) are listed in Table 1. From which it is clear that the cubic lattice parameter  $a$  increases with an increase in yttrium content for all the compositions. This increase in lattice parameter is due to the replacement of smaller  $\text{Al}^{3+}$  ions ( $0.53 \text{ \AA}$ ) with larger  $\text{Y}^{3+}$  ions ( $0.90 \text{ \AA}$ ) which causes dilation of the spinel lattice and results in increase of the lattice parameter. The trend in the values of X-ray density ( $d_{\text{X-ray}}$ ) is mirror image of the trend shown by the lattice parameter. Density of the doped samples is more than that of the pure nickel aluminate due to the higher atomic mass of yttrium (88.906) than that of aluminum (26.982) [14].

The influence of yttrium concentration on crystallite size ( $D$ ) is tabulated in Table 1. It decreases with an increase in yttrium content. It is an established fact that the crystallites of small size produce broadened diffraction peaks and too have small number of parallel diffraction planes [13]. A possible reason for the decreasing trend of crystallite size is that the increasing concentration of yttrium limits the continuation of ordering process among different planes. This is probably due to diffusion of some of the  $\text{Y}^{3+}$  ions into the diffraction planes which hampers their growth mechanism, thereby decreasing the crystallite size. Few representative TEM images have been taken to measure the particle size as shown in Fig. 2. These micrographs reveal that the particle size is larger than the crystallite size calculated from the XRD listed in Table 1, which suggests that the nanoparticles are formed due to aggregation of different crystallites. The selected area electron diffraction pattern (SAED) of the samples ( $x = 0.00, 0.05$ ) are shown in Fig. 3. This figure demonstrates the polycrystalline nature of the samples and is indexed to the cubic spinel structure of the nanoparticles.

The FTIR patterns of  $\text{NiAl}_{2-2x}\text{Y}_{2x}\text{O}_4$  series confirm the formation of spinel structure from the appearance of bands around  $740\text{ cm}^{-1}$  ( $\nu_1$ ) and  $500\text{ cm}^{-1}$  ( $\nu_2$ ) Fig. 4. These bands are attributed to the stretching vibrations of Al–O in tetrahedral and octahedral coordination states respectively, which are characteristic for spinel [15]. All the samples also contain common absorption bands around  $3430\text{ cm}^{-1}$  and  $1630\text{ cm}^{-1}$ . These bands can be assigned to OH antisymmetric stretching and H–O–H bending mode respectively, which may be caused by moisture absorbed from the air during the pressing of pellets. Moreover a careful investigation of the FTIR

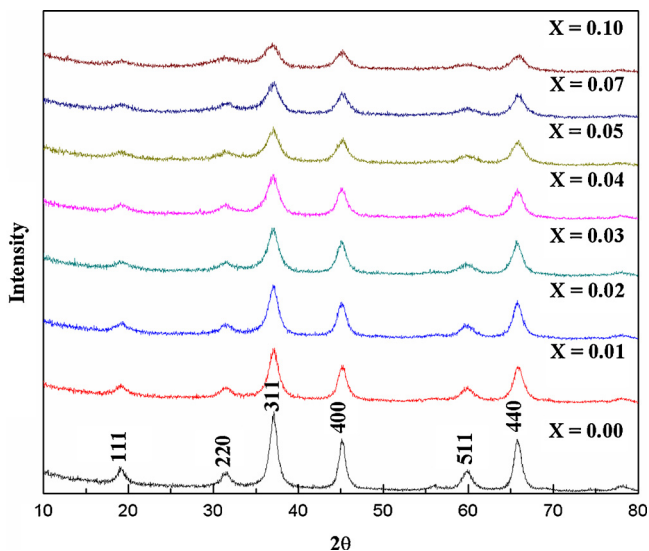


Fig. 1. X-ray diffraction patterns of  $\text{NiAl}_{2-2x}\text{Y}_{2x}\text{O}_4$  ( $x = 0.00$ – $0.10$ ) system.

Download English Version:

<https://daneshyari.com/en/article/10639859>

Download Persian Version:

<https://daneshyari.com/article/10639859>

[Daneshyari.com](https://daneshyari.com)