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VARIABLE RANGE HOPPING CONDUCTION IN NiO/Al_2O_3 NANOCOMPOSITES

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The formation and electrical properties of high surface area NiO/Al_2O_3 nanocomposite materials with composition ranging from 5 to 30% w/w have been studied. The temperature dependence of the DC electrical resistivity was monitored in the temperature range 350–600 K. The results revealed correlation between electrical resistivity and textural properties. The conductivity results were discussed in terms of variable-range-hopping mechanism.

Keywords: NiO/Al_2O_3; nanocomposite; polaron conduction.

1. Introduction

Nano- and microstructured materials have been recently the subject of intense research due to their extraordinary physical and physicochemical properties.[1–3] NiO/alumina represent a very important system which find many diverse application.[2,3] Various techniques have been developed to prepare these materials, among them sol–gel method was very promising. In particular, we have recently prepared NiO/Al_2O_3 nanocomposites and reported their humidity sensing properties.[4]

The conductivity of various glasses and glass ceramics containing transition metal (TM) oxides, e.g., Fe_2O_3 or NiO is mainly carried out by polarons.[5,6] In nanostructured NiO thin film, the logarithm of electric resistivity ($\log \rho$) was found to scale with $(1/T)^{1/4}$, indicating variable range hopping of charge carriers between randomly distributed localized electronic states in the NiO sample.[7] The electrical resistivity in NiO/SiO_2 nanocomposite films obtained by oxidation treatment of nickel–silica is explained in terms of a phonon-assisted small polaron hopping in

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the amorphous phase that comprise the interface between nanosized NiO layers.[8] In this paper, we explore the dispersion of NiO nanoparticles in fibrous alumina matrix and measure the electrical properties of their composites.

2. Experimental

5–30% w/w NiO/Al_2O_3 nanocomposites were prepared via a sol–gel method, which involved mixing of the respective sol–gel precursors, followed by drying and calcination at 873 K for 3 h as described elsewhere.[4] For simplicity, the respective code numbers 605, 610, 620, and 630 are designated for the test materials containing 5, 10, 20 and 30% w/w NiO/Al_2O_3.

The samples for electric measurements were shaped into pellets of 1.0 mm thickness and 13 mm diameter. The disc was held between gold–coated electrodes with very slight spring pressure in a sample holder constructed from Teflon. DC electrical measurements were performed under low Argon pressure by using a 617 Keithley electrometer. The temperature is measured using a K-type thermocouple and a PM2525 Philips digital multimeter.

3. Results and Discussion

Figure 1 shows the dependence of the DC electrical resistivity of the studied NiO/Al_2O_3 nanocomposites on the NiO content at indicated temperatures. The resistivity increases with increasing NiO content from 5 to 10% and decreases with further increase of NiO above 10%. The behavior can be understood in view of

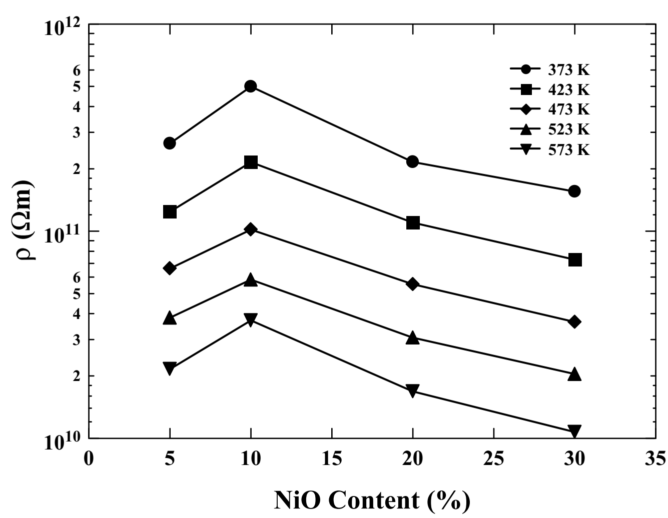

Fig. 1. Dependence of the electrical resistivity of NiO/Al_2O_3 nanocomposites on NiO content at indicated temperatures.

the morphological changes of the specimens when the NiO content is changed. The relative resistivity of the samples were in the order No. 605 < No. 610 > No. 620 > No. 630. This order is exactly the same for the BET specific surface area (S_{BET}) values, which were in the order No. 605 < No. 610 > No. 620 > No. 630.[4]

The dependence of the electrical resistivity ρ on temperature for all samples was measured. The $\log \rho$ versus $1000/T$ plot was nonlinear for all samples. Various theoretical models used to explain the DC conductivity data of TM oxides have been examined by several investigators. Among them, the pair correlation-type model of Mott has been extensively used. If the charge carriers responsible for conduction are small polarons, the temperature dependence of the DC resistivity due to hopping of small polarons can be described by:

$$\rho(T) = \rho_0 T \exp\left(\frac{W}{k_B T}\right), \quad (1)$$

where ρ_0 is the pre-exponential term, W the activation energy for the involved process, T the absolute temperature and k_B the Boltzmann's constant.[9,10] In similar systems, e.g., NiO/SiO_2 nanocomposite films and CuO:SiO_2 glasses, it has been shown that the temperature-dependence of the DC electrical resistivity can be well-explained by adapting a phonon-assisted small polaron hopping mechanism.[8,11]

In view of this model, the conductivity is assumed to occur via adiabatic hopping, therefore the resistivity can be expressed by a formula proposed by Austin and Mott,[9,10] which reads as:

$$\rho(T) = \frac{k_B T R}{\upsilon_0 C(1-C)e^2} \exp(2\alpha R) \exp\left(\frac{W}{k_B T}\right), \quad (2)$$

where υ_0 is the characteristic phonon frequency of the lattice, C is the fraction of the Ni^{++} concentration, α^{-1} the localization length describing the localized state of each transition metal, R the intersite separation and W is the activation energy of the electron-site interaction and/or the static disorder and can be expressed as:

$$W = W_H + \frac{1}{2} W_D \quad \text{for} \quad T > \theta_{D/2} \quad \text{and} \quad W = W_D \quad \text{for} \quad T < \theta_{D/4}\,, \quad (3)$$

where W_H is the polaron hopping energy, W_D is the disorder energy arising from the energy difference between two hopping sites , θ_D is the Debye temperature and ρ_0 in Eq. (1) is given as:

$$\rho_0 = \frac{k_B R}{\upsilon_0 C(1-C)e^2} \exp(2\alpha R)\,.$$

$\log \rho$ was first fit using a linear form to estimate W and then the W value is inserted in Eq. (2) and all other parameters are taken free in the fitting procedure. The solid lines in Fig. 2 are the computer fits to the experimental data. The fit parameters are displayed in Table 1.

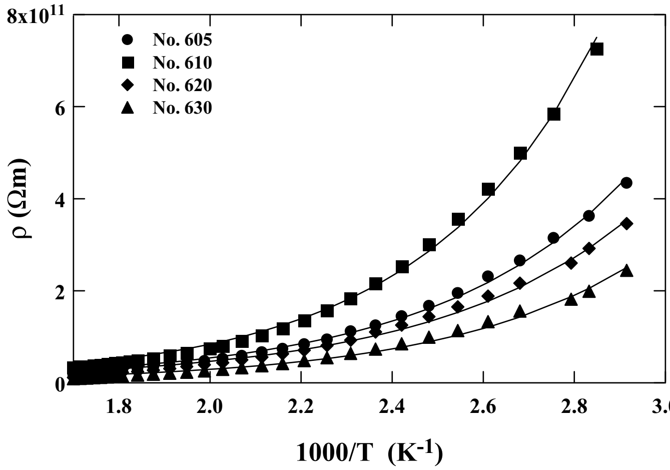

Fig. 2. Variation of resistivity as a function of inverse temperature of NiO/Al_2O_3 nanocomposites. The solid lines are the computer fits.

Table 1. Resistivity fit parameters for NiO/Al_2O_3 nanocomposites.

No.	W (eV)	α ($Å^{-1}$)	R (Å)	C	v_0 (s^{-1})	r_p (Å)	ε_p	W_H (eV)	W_D (eV)	$N(\varepsilon_F)$ $eV^{-1}\,cm^{-3}$
605	0.23	4.50	3.09	0.94	8.1×10^{12}	1.248	12.33	0.139	0.190	2.17×10^{19}
610	0.26	4.50	3.09	0.94	8.5×10^{12}	1.247	11.16	0.154	0.208	1.48×10^{19}
620	0.23	4.51	3.10	0.94	8.3×10^{12}	1.249	12.72	0.135	0.182	2.15×10^{19}
630	0.24	4.48	3.07	0.93	9.7×10^{12}	1.239	12.21	0.141	0.190	1.94×10^{19}

Using the simple electrostatic principle, Austin and Mott[12] showed that:

$$W_H = \frac{e^2}{4\varepsilon_p}\left[\frac{1}{r_p} - \frac{1}{R}\right], \tag{4}$$

where r_p is the polaron radius and ε_p is effective dielectric constant. The small polaron radius can be calculated from:

$$r_p = \frac{1}{2}\left(\frac{\pi}{6}\right)^{1/3} R\,. \tag{5}$$

We have obtained the values of r_p for all specimens using R values obtained from the fit. According to Austin and Mott, the polaron binding energy W_p is given by:

$$W_p = \frac{e^2}{2\varepsilon_p r_p}\,.^{12} \tag{6}$$

The value of ε_p can be calculated from Eq. (6) by considering $W_p = 2W$, giving

$$\varepsilon_p = \frac{e^2}{4W r_p}\,.^{13} \tag{7}$$

The r_p and W values thus obtained are substituted in Eq. (7) to obtain a value of ε_p ranging from 11 to 13 for all specimens. The rather large values of $C > 0.92$ for all specimens arises due to the fact that the measurements are performed under low Argon atmosphere, in which case the fraction of lower valence nickel ions (Ni^{2+}) would become very large. Using the estimated values of W_H, one can obtain values of W_D. The conductivity parameters, namely r_p, ε_p, W_H and W_D, are displayed in Table 1.

At low temperature and in view of Mott, the conductivity is controlled by the variable-range-hopping (VRH) mechanism. Accordingly, the resistivity is given as:

$$\rho(T) = A \exp\left(\frac{B}{T^{1/4}}\right), \tag{8}$$

where A is a constant, $B = 2.14\left[\alpha^3/k_B N(\varepsilon_F)\right]^{1/4}$ and $N(\varepsilon_F)$ is the density of energy states at the Fermi level.[10]

The VRH mechanism normally occurs only in the low temperature region (below room temperatures), wherein the energy is insufficient to excite the charge carriers across the coulomb gap. Hence the conduction takes place by hopping of small region ($\sim k_B T$) in the vicinity of Fermi energy (ε_F). In this region, the density of states remains almost constant. Recent studies have shown that the VRH mechanism occur over a fairly wide temperature range (100–900 K).[14,15] Moreover, VRH mechanism has been shown to be responsible of the conduction in pure NiO thin films and nanoparticles.[7,16] As shown in Fig. 3, the linear dependence of $\log\rho$ on $1/T^{1/4}$ is perfectly obtained for $T < 550$ K showing that Eq. (8) best describes the electrical resistivity data of the present system. The $N(\varepsilon_F)$ is obtained for all samples from the constant B and is listed in Table 1. In view of this model, the

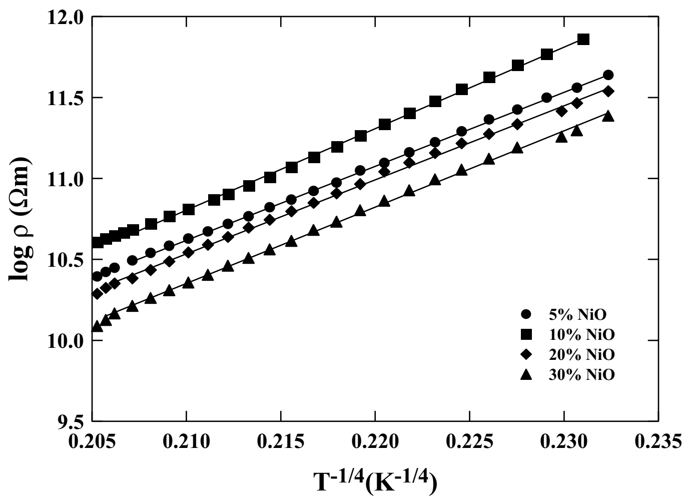

Fig. 3. Dependence of $\log\rho$ on $1/T^{1/4}$ of NiO/Al_2O_3 nanocomposites. The solid lines are the linear fits for $T < 550$ K.

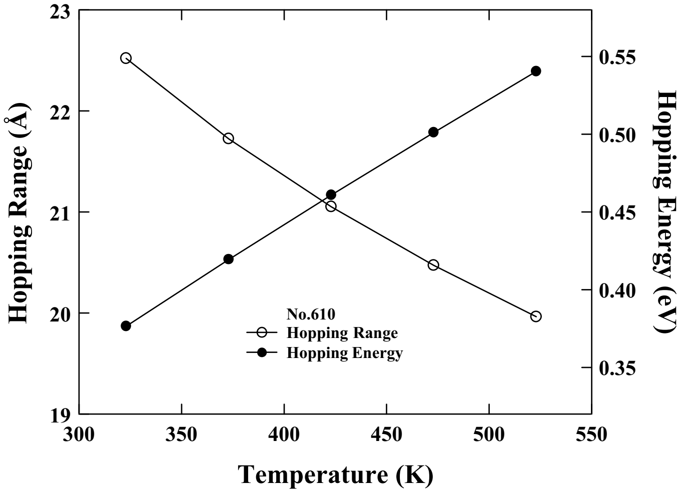

Fig. 4. Dependence of hopping range and energy on temperature for $T < 550\,\mathrm{K}$.

hopping range (R_H) and hop energy (W_H) are given as $R_H = [3/2\pi\alpha N(\varepsilon_F)k_BT]^{1/4}$ and $W_H = 3/4\pi R_H^3 N(\varepsilon_F)$.

The estimated values of R_H ad W_H are presented in Fig. 4 as functions of temperature for the 10% NiO/Al_2O_3 sample. As shown in Fig. 4, the hopping distance decreases with increasing temperature. This is due to the increase in disorder in the system so that conduction takes place via hopping of carriers to states located close in space to the initial state. This normally leads to trapping of carriers and hence to the formation of small polarons. On the other hand, the hopping energy increases with increasing temperature. This implies that with the increase in disorder, in the system, more energy is required for carriers to make a transition to the final state, but with large energy.

4. Conclusion

DC electrical resistivity in NiO/Alumina nanocomposites was studied in the temperature range 350–600 K. The correlation between electrical resistivity and textural properties is obtained. The conductivity results were discussed in terms of variable-range-hopping mechanism.

Acknowledgment

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