CeO₂/NiTiO₃ nanocomposites; synthesis, photoluminescence and magnetic behavior

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Pure phase NiTiO₃ was obtained via a modified sol-gel method. Addition of CeO₂ in a modified oxidizing atmosphere in stearic acid at 750 °C led to the growth of several nanoscaled Ce-rich phases. The formation of NiTiO₃ and CeO₂/NiTiO₃ was strongly confirmed based on metal-oxygen and metal-metal absorption bands. The nanometric formation of crystals and narrow distribution of nanoparticles were confirmed by XRD and FE-SEM. The magnetic properties indicated weak ferromagnetic behavior of NiTiO₃ and paramagnetic behavior of CeO₂/NiTiO₃ nanocomposites. The paramagnetic properties were improved gradually into superparamagnetic upon increasing CeO₂ domain to 30 mol%. It was observed that the current density can achieve 1×10^{-9} A/cm² for the sample containing 30 mol% CeO₂ at an electrical field equal to 40 V/cm.

Keywords: NiTiO₃; sol-gel; magnetic behavior; nanocomposite

1. Introduction

3d-metal monoxides like MnO, FeO, CoO and NiO are semiconductors with low electrical conductivities. In general, the mentioned metal oxides have so large band gaps that they are insulators [1].

Many applications of multi-metal oxides have been reported in electrodes of solid oxide fuel cells, metal-air barriers, gas sensors and high performance catalysts [2–11]. Nickel containing mixed metal oxide is one of the most attractive materials that have been widely investigated. Zn-doped NiFe₂O₄ [12], NiMoO₄ [13], Ni_xMn_{3-x}O₄ [14], Ni_xZn_{1-x}Fe₂O₄ [15], Ni_{1-x}Co_xFe₂O₄ [16] are some examples of the mentioned materials where A site is occupied by Ni cations. Among them, nickel titanate has been investigated as a tribological coating to reduce friction and wear at high temperature [17–20].

Nickel titanate, NiTiO₃, has a perfect ilmenite structure at high temperatures. Generally, the compounds with ilmenite structure in trigonal system are important as chemical and electrical materials

due to their weak magnetism and semiconductivity. However, traditional synthesis of NiTiO₃ at room temperature results in a lower symmetry, tetragonal unit cell with inhomogeneous and large NiTiO₃ particles [21]. Several methods are generally used to synthesize mixed metal oxides like ilmenites, perovskites, etc. [22]. However, sol-gel technique is accepted as a promising process for production of materials with sufficiently well-controlled structural properties. In general, sol-gel process can provide several important advantages such as low synthesis temperature, high purity of obtained materials, versatility of control over the nature of an interface, convenience of obtaining new properties of resulting materials [23].

Semiconducting properties of CeO_2 have been rarely studied in terms of its using as a material for solar cells, photocatalysis, and organic photovoltaics. CeO_2 is a non-toxic electroactive material which can be used as a dopant/modifier to enhance the electroactive surface area of under loading materials. It can impart unique properties such as mechanical strength, oxygen ion conductivity, high isoelectric point, biocompatibility and high adsorption capability as well as oxygen storage capacity in a final product.

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Fig. 1. A scheme of preparation of CeO₂/NiTiO₃ nanocomposites.

Introducing of dopants like CeO₂ during a solgel process is an acceptable route for production of functional materials. Such a compound offers enhanced properties of mixed metal oxides.

In this study, a typical wet chemistry synthesis method was selected for preparation of $CeO_2/NiTiO_3$ nanocomposites. It was found that introducing of CeO_2 in NiTiO_3 can change the properties (magnetic and conducting) of pure NiTiO_3 for further industrial applications.

2. Experimental

2.1. Materials and method

NiTiO₃ powders were prepared according to the synthetic procedure shown in Fig. 1. Nickel stearate, tetrabutyl titanate, and stearic acid (Merck-Germany) were used as received. An appropriate amount of stearic acid was primarily melted in a beaker at around 73 °C. A fixed amount of nickel stearate was added to the melted stearic acid to form a green transparent solution. Stoichiometric amount of tetrabutyl titanate was added slowly into the solution, followed by stirring to obtain a homogeneous light green sol that was naturally cooled down to room temperature and dried in an oven for 12 h (dried gel). This gel was finally calcined in air to form nanosized NiTiO₃.

In the next step of $CeO_2/NiTiO_3$ nanocomposites preparation, 10 mol%, 20 mol% and 30 mol% of cerium butoxide was added into a mixture of nickel stearate and tetrabutyl titanate in melted stearic acid to gain a homogeneous sol that was dried in an oven for 12 h (dried gel), and calcined at 750 $^{\circ}$ C.

2.2. Characterization

CeO₂/NiTiO₃ Spectroscopic analyses of nanocomposites were carried out using The XRD PerkinElmer FT-IR spectrometer. patterns of the products were recorded using a PTS 3003 SEIFERT diffractometer (UK) (CuKa radiation, $\lambda = 1.5418$ Å) in the 2 θ range between 10° and 80° to examine the structural phase evolution of NiTiO₃ and its respective nanocomposites.

Field emission scanning electron microscopy (FE-SEM), using a JEOL (Japan) microscope was used to observe the size and morphology of the samples. The quantitative elemental analysis was performed using energy dispersive X-ray spectra (EDX-HITACHI ZAF-Japan) to confirm the sample structure.

Magnetization measurements of NiTiO₃ and $CeO_2/NiTiO_3$ nanocomposites were performed using vibrating sample magnetometer (VSM-BHV-55, Riken, JAPON) at room temperature.

The emission of photoluminescence radiation was studied with a luminescence spectrometer, LS-5, PerkinElmer. Excitation was provided by a pulsed xenon discharge lamp at 250 nm, with a standard source monochrometer (scanning range of 200 nm to 800 nm). Conductivity of NiTiO₃ and $CeO_2/NiTiO_3$ nanocomposites was analyzed using KEITHLEY 236 Source MEASURE Unit.

3. Results and discussion

3.1. Structural analysis

NiTiO₃ and CeO₂/NiTiO₃ nanocomposites were investigated using FT-IR to detect their structures. The NiTiO₃ nanoparticles show a number of vibration frequencies below 800 cm^{-1} . These absorption bands can be related to the metal-oxygen characteristic bands, i.e. Ni-O and Ti-O vibration frequencies. A characteristic band at around 465 cm^{-1} in the spectrum of undoped material indicates the metal-metal (Ni-Ti) vibrational frequency. Moreover, two bands at 570 cm^{-1} and 618 cm^{-1} can be attributed to the asymmetric stretching modes of TiO₂. The FT-IR spectrum of NiTiO₃ has been discussed elsewhere [18]. The spectra of 10 mol% and 30 mol% CeO₂ doped nanocomposites (Fig. 2) indicate two peaks at 3419 cm^{-1} and 2345 cm^{-1} , corresponding to the presence of -OH and CO₂ residues from atmospheric contaminants. The band at 1638 cm^{-1} can refer to the bending mode of water. Two important characteristic bands of nickel titanate can be observed at 550 cm^{-1} and 456 cm^{-1} for the sample containing 10 mol% CeO₂. However, upon increasing CeO₂ concentration up to 30 mol%, these peaks are shifted slightly into the lower frequencies, 545 cm⁻¹ and 439 cm⁻¹.

Fig. 3 shows the XRD patterns of NiTiO₃ and CeO₂/NiTiO₃ nanocomposites after heat-treatment at 750 °C in air. To extract the comparable quantitative structural and lattice information of the nanocomposites, all the samples were exposed to the X-ray radiation (Fig. 3).

The number and the positions of the diffraction maxima of rhombohedral NiTiO₃ nanopowders (Fig. 3a) are well matched with the compiled database JCPDS Card No. 33-960, indicating a pure and fine crystalline structure of the samples.

Upon increasing CeO_2 in the NiTiO₃, the crystal structure of CeO_2 is also displayed in the X-ray



Fig. 2. FT-IR spectra of (a) 10 mol% and (b) 30 mol% CeO₂/NiTiO₃.



Fig. 3. X-ray diffraction patterns of CeO₂/NiTiO₃ nanocomposites containing (a) 0 mol%, (b) 10 mol%, (c) 20 mol% and (d) 30 mol% CeO₂.

diffractograms and the positions of intense peaks of neat NiTiO₃ are slightly shifted. However, the peak positions can still be matched with the powder diffraction data for pure NiTiO₃ (JCPDS Card No. 33-960). In the sample containing 10 mol% CeO₂ (Fig. 3b), the pure structural patterns of $NiTiO_3$ are dominating. It must be mentioned that the pure CeO_2 has been compiled into the database by the JCPDS Card No. 34-0394 [24].

Continuous increase in CeO_2 to 20 mol% (Fig. 3c) and 30 mol% (Fig. 3d) does not cause any significant changes in the compound structure, and the CeO_2 phases are well-promoted and dispersed in the fine structure of ilmenite.

The average grain size was determined from XRD powder patterns according to the Scherrer's equation 1:

$$D = k\lambda / \beta \cos\theta \tag{1}$$

where D is an average grain size, k is a constant equal to 0.9, λ is the X-ray wavelength equal to 0.15406 nm and β is the half-peak width. The crystallite size has been calculated for various mol% fractions of CeO₂/NiTiO₃ nanocomposites (Table 1). It is obvious that upon increasing CeO₂ concentration, the average grain size decreases from 69 nm to 55 nm. This is because of inhibition effect of CeO₂ on the formation of NiTiO₃ agglomerates.

Table 1. Average grain size of NiTiO₃ and its respective nanocomposites.

CeO ₂ [mol%]	0	10	20	30
D [nm]	50	69	61	55

Fig. 4 shows the surface microstructure (FE-SEM images) of 10 mol% CeO₂ doped sample (at two magnifications) calcined at 750 °C. The morphology demonstrates some extent of agglomerated areas randomly distributed in the sample. The shape of the particles is semi-spherical with the average particle size about 73 nm. The elemental analysis of 10 mol% CeO₂ doped NiTiO₃ nanocomposite under the energy dispersive X-ray spectra (EDX) confirms the presence of Ni, Ti, Ce and O in the sample. The results indicate that the relative atomic ratios are close to the expected values. It is suggested that the experimental values of the atomic percentages are well matched with the stoichiometry amounts taken during preparation.







Fig. 4. FE-SEM micrographs at two different magnifications (a) 43×, (b) 19000× and (c) EDX analysis of 10 mol% CeO₂/NiTiO₃ nanocomposite.



Fig. 5. VSM curves of CeO₂/NiTiO₃ nanocomposites containing (a) 0 mol%, (b) 10 mol%, (c) 20 mol% and (d) 30 mol% CeO₂.

3.2. Magnetic properties

Fig. 5 shows magnetization of NiTiO₃ and its respective nanocomposites. The curve of magnetization of pure NiTiO₃ shows a weak ferromagnetism at room temperature (Fig. 5a) [25].

Upon increasing CeO₂ concentration, the magnetization diminished most probably due to the effect of magnetic force agitation. This can also be observed in 10 mol% CeO₂/NiTiO₃ nanocomposites (Fig. 5b). The ferromagnetic behavior can be attributed to the presence of magnetic ions mediated by oxygen vacancies [24].

In the sample with 20 mol% CeO₂ (Fig. 5c), a paramagnetic behavior can be observed. The reduced M_r (room temperature remnant magnetization) and H_c (magnetic coercivity) values are close

to one of the characteristics of superparamagnetic responses. The CeO₂/NiTiO₃ sample containing 30 mol% CeO₂ (Fig. 5d) indicates a superparamagnetic behavior. This is because of zero coercivity and remanence on the magnetization loop [26]. In a superparamagnetic system, particles do not show hysteresis in the M-H curves; hence H_c and M_r are near zero [27–29].

3.3. Photoluminescence

The photoluminescence (PL) spectra of NiTiO₃ and CeO₂/NiTiO₃ nanocomposites are shown in Fig. 6. The NiTiO₃ nanoparticles exhibit several peaks situated at 398 nm, 410 nm, 423 nm, 444 nm, 461 nm, 487 nm and 530 nm. The absorption peak situated at around 410 nm is associated with O_2/Ti^{4+} charge transfer transitions.



Fig. 6. Photoluminescence spectra of NiTiO₃ and various CeO₂/NiTiO₃ nanocomposites.

The higher wavelength shoulder is associated with the crystal field splitting of NiTiO₃, giving rise to the Ni²⁺/Ti⁴⁺ transitions [30].

The PL spectrum of CeO_2 nanoparticles shows several strong emission bands in the blue-green region of visible range, one at 469 nm and three peaks at 452 nm, 483 nm, and 493 nm. The emission bands located between 400 nm and 500 nm can be attributed to the defect levels of Ce-4f to O-2p bands. The strong emission at 469 nm is most probably due to the abundant defects [31].

The 10 mol% CeO₂ doped NiTiO₃ shows a sharp peak at 424 nm and a weak peak in the green band at 488 nm. The intensities of both peaks are relatively higher than those in pure NiTiO₃ sample.

In the sample with 20 mol% of dopants, the two maxima are observed at 424 nm and 489 nm. These

two maxima in the sample containing 30 mol% CeO_2 can also be observed, however, the position of the third maximum is located at 448 nm.

The PL results indicate that the two maxima are observed in all the samples. Upon the stepwise increasing of CeO₂ concentration from 10 mol% to 30 mol%, the luminescence efficiency has first increased at 10 mol% of CeO₂ and then decreased at 20 mol% and 30 mol%. Sahoo et al. [32] reported a similar behavior, which is in agreement with the general theory implying that luminescence efficiency first increases and then falls gradually with dopant concentration. It must be noted that some of the CeO₂ and NiTiO₃ peaks are overlapped.

3.4. Electrical conductivity

The electrical conductivity of $NiTiO_3$ and its respective nanocomposites are shown in Fig. 7.

The I-V characteristic were obtained at room temperature for a pellet with a diameter of 0.99 cm and thickness of 0.180 cm. The results indicate that all the samples show a semiconducting behavior in air at room temperature. The results strongly support the Bohnke report [33] on a synthesis of $Li_{3x}La_{2/3-x}TiO_3$ prepared by a modified Pechini method.



Fig. 7. Electrical conductivity of NiTiO₃ and various CeO₂/NiTiO₃ nanocomposites.

Upon increasing CeO₂ mol%, the current density has also increased. For example, in the sample with 30 mol% CeO₂, at electrical field of 40 V/cm, the current density is the highest ($\sim 1 \times 10^{-9}$ A/cm²). This phenomenon cannot be observed in pure NiTiO₃. The large variation in the current suggests that the sample could provide high sensitivity when operated as an optically controlled switch.

It can be concluded that the samples, such as $30 \text{ mol}\% \text{ CeO}_2/\text{NiTiO}_3$ nanocomposite, can be used in the devices fabricated for dual functionalities, tribological properties and partial current density (J) at room temperature at a depressed voltage (V).

4. Conclusions

This study has demonstrated the feasibility of synthesis of crystallized $CeO_2/NiTiO_3$ nanocomposites using a modified sol-gel synthesis method at 750 °C. The average crystallite size in 10 mol%

CeO₂/NiTiO₃ nanocomposites was about 73 nm. It was confirmed by XRD results. NiTiO₃ has showed a weak ferromagnetic behavior, as evidenced by VSM measurements at room temperature. Moreover, luminescence efficiency of the sample containing 10 mol% of CeO₂ was higher than that of the other nanocomposites. In the sample with 30 mol% CeO₂, the current density achieved the highest value at 40 V/cm E.F. On the other hand, the large variation in the current doting suggests that the sample could provide high sensitivity when operated as an optically controlled switch.

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