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Thermo-optical effect of $Nd_{0.3}Sm_{0.7}NiO_3$ ceramic in the infrared range

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ABSTRACT

$Nd_{0.3}Sm_{0.7}NiO_3$ exhibits a reversible metal semiconductor phase transition which is, in the infrared range, responsible of a thermo-optical contrast. The variation of the thermal emittance for $Nd_{0.3}Sm_{0.7}NiO_3$ ceramic was measured, in the mid-infrared range, by using reflectance measurements and on a benchtest. The thermo-optical effect of the sample was measured in situ by thermal imaging camera. The emissivity contrast obtained is 18% between 293 and 373 K which induced a difference of 27 K between the real and the visible temperature at 373 K.

1. Introduction

The transition metal oxide materials are finding civil or military applications where it is interesting to have a thermochromic switching in infrared range [1]. In the infrared window, where a thermal imaging camera used as a detector (8–12 μm), the emittance of the object plays an important role for precise measurements.

To be infrared-invisible, the object must adapt its emittance to the background's one. An interesting situation occurs when two materials have their temperature and their emissivity which compensate each other with the aim of having the same emittance. Under these conditions, the thermal imaging camera can not distinguish the two objects. The situation would be more interesting if the emissivity of the material can be adjusted with the temperature of the background (For more details, see [2]). For this situation, temperature – switching materials in the infrared range seem to be extremely interesting. Further studies have shown the potentiality of the rare-earth nickelate (general formula $RNiO_3$, R is a rare-earth) as thermochromic materials due to the transition temperature which can be adapted by changing the rare-earth [3–6].In this work, the characterizations of infrared reflectivity, emissivity and thermal imaging are presented.

2. Sample preparation

The polycrystalline sample $Nd_{0.3}Sm_{0.7}NiO_3$ was prepared by modified sol–gel method adapted from A. Douy [7] by using NiO, Sm_2O_3 and Nd_2O_3 precursors. The oxides were dissolved in nitric acid. Appropriate amounts of each solution were mixed in stoichiometrical proportions and citric acid was added as chelating agent. At 80 °C, acrylamide and N-N'-methylenediacrylamide was added in order to form a three dimensional gel. The polyacrylamide gel obtained was calcined at 300 °C for 2 h, then at 650 °C during 5 h in a furnace producing a spongy material that, after annealing at 700 °C for 12 h, formed a dark gray fine powder. To obtain high-quality sample and to stabilize Ni^{3+}, the sample was heat-treated twice at 790 °C under 175 bars of oxygen pressure during 12 h. Then, the powder was pressed into pellets and sintered under the same conditions.

3. Structural characterizations

The powder X-ray diffraction pattern was collected at room temperature on a Rigaku Miniflex diffractometer using Cu K_α radiation ($\lambda = 1.5418$ Å). Diffraction pattern was recorded in the 2θ range 10°–90° (step $\Delta\theta = 0.02$). The X-ray data analysis was performed with the Rietveld method using pseudo-Voigt function. The thermogravimetric analysis is used to determine the oxygen rate in the structure by reducing the material under a flowing mixture of H_2 3% / Ar 20% / N_2. The thermogravimetric curve was obtained on a Perkin Elmer TGA 7 thermogravimetric analyser,

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working at a heating rate of 1.5 Cmin^{-1}. About 40 mg of sample was used in this experiment.

4. Methods to measure the emissivity

Numerous methods can be used to measure the emissivity. We have used two different ones. The first one consists of deducing the emissivity from the reflectivity spectra. This indirect measurement is carried out with a Nicolet Magna 860 spectrophotometer equipped with an integrating sphere (Hemispherical Directional Reflectometer SOC 100) which includes the specular and the diffuse parts of the reflectivity. For the $Nd_{0.3}Sm_{0.7}NiO_3$ ceramic, which is an isothermal system and at thermal equilibrium, we have applied the conservation principle of the flux (1) and the Kirchoff's law (2) to link the reflectivity to the emissivity.

$$\rho + \tau_\lambda + \alpha_\lambda = 1 \tag{1}$$

where ρ_λ, τ_λ and α_λ are the spectral reflectance, the spectral transmittance and the spectral absorbance of the flow respectively. The $Nd_{0.3}Sm_{0.7}NiO_3$ ceramic is an opaque sample ($\tau_\lambda = 0$), the previous equation gives $\alpha_\lambda = 1 - \rho_\lambda$.

The Kirchoff's law is used to link the spectral reflectance to the spectral emissivity.

$$\alpha_\lambda = 1 - \rho_\lambda = \varepsilon_\lambda \tag{2}$$

where ε_λ is the monochromatic emissivity.

The calculus of integrated emissivity on the working – field of the infrared detectors was made from the infrared reflectance spectra by using the following equation:

$$\varepsilon_{\Delta\lambda} = \frac{\int_{\lambda_1}^{\lambda_2}(1-\rho(\lambda))M^0(\lambda,T)d\lambda}{\int_{\lambda_1}^{\lambda_2}M^0(\lambda,T)d\lambda} \tag{3}$$

where $M^0(\lambda,T) = \frac{2hc_0^2\lambda^{-5}}{\exp(\frac{hc_0}{k\lambda T})-1}$ is the luminance of the black body (h is the Planck's constant, k is the Boltzmann's constant, c_0 is the light celerity, λ is the wavelength and T is the temperature).

The second method consists of measuring the emissivity on a directional benchtest. The integrated emissivity measurements were carried out, on heating and on cooling in air, in the 8–12 μm wavelength range, using an HgCdTe infrared detector. The emissivity data were calibrated by comparing the sample optical response to a black body.

5. Thermo-optical measurements

The thermo-optical effect of the $Nd_{0.3}Sm_{0.7}NiO_3$ ceramic was in situ measured by using a thermal imaging camera Cedip Jade 3 BB F working in the 8–12 μm range (detector HgCdTe). The sample was heated from 20 °C to 100 °C and maintained at this temperature for 10 min. To measure the thermo-optical effect in situ, the sample emissivity is fixed and considered as independent of the temperature.

6. Results and discussions

6.1. X-ray diffraction

The X-ray diffraction experiments on the ceramic confirm the synthesis of single phase material, only showing the perovskite structure characterized by intense reflections in 2θ equal to 23.34°, 33.24° and 47.64°. All peaks of the X-ray pattern were indexed with the orthorhombic distorted perovskite and Pbnm space group (Fig. 1) according to Frand et al. [8]. The actual Sm substitution by Nd was inferred by the changes observed in the (022) and (202) peaks in comparison with $SmNiO_3$. The data reveal a shift of the reflection to lower 2θ values due to the substitution of Sm^{3+} by a larger Nd^{3+} ion (Fig. 1). X-ray data analysis was performed with the Rietveld method. Cell's parameters refined are a = 5.352 Å, b = 5.422 Å, c = 7.589 Å and V = 220.20 Å and are in good agreement with literature [8].

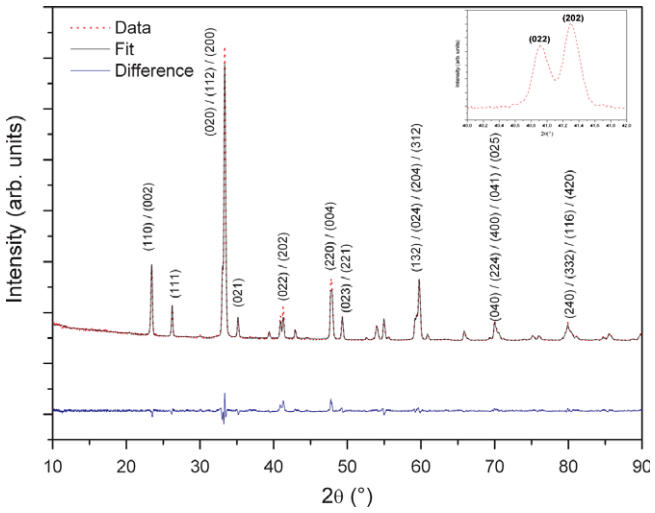

Fig. 1. X-ray diffraction pattern of $Nd_{0.3}Sm_{0.7}NiO_3$ ceramic. In insert, the (022) and (202) peaks showing the Sm substitution by Nd in the structure $SmNiO_3$.

6.2. Thermogravimetric analysis

The effect on oxygen nonstoichiometry on the transport properties of the $NdNiO_{3-\delta}$ compounds have been already studied by Nikulin et al. [4]. In fact, an oxygen deficit in the structure causes a decrease of the resistivity contrast between the insulator state (below the T_{MI}) and the metallic state (up the T_{MI}) which may induce changes in optical properties. Thermogravimetric analysis is used to control the oxygen rate in the structure by reducing the $Nd_{0.3}Sm_{0.7}NiO_3$ under H_2/N_2 flow. Fig. 2 shows the thermogravimetric profile of $Nd_{0.3}Sm_{0.7}NiO_3$ sample. The curve suggests that

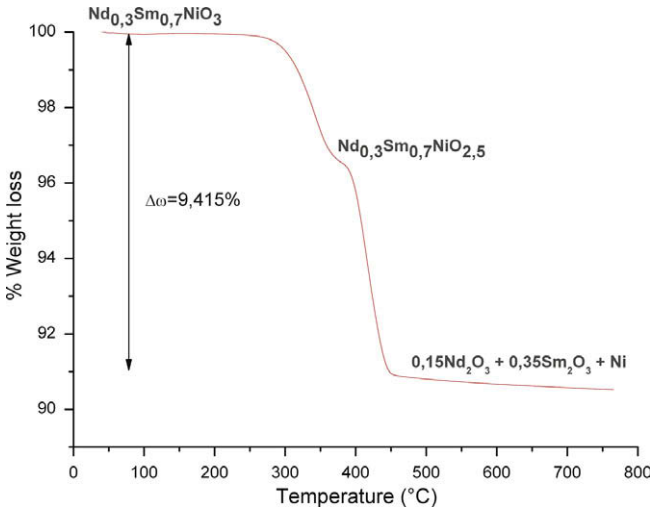

Fig. 2. Thermal analysis (TG) curves of $Nd_{0.3}Sm_{0.7}NiO_3$ ceramic grinded under reducing conditions (H_2/N_2 flow).