Prediction of thermal radiative properties (300–1000 K) of $La_2NiO_{4+\delta}$ ceramics

M. T. Ta,[1] J. Y. Rolland,[1] P. Echegut,[1] B. Rousseau,[1,a)] M. Zaghrioui,[2] F. Giovannelli,[2] H. Gomart,[3] P. Lenormand,[4] and F. Ansart[4]
[1]*CEMHTI CNRS, UPR 3079, 1D avenue de la Recherche Scientifique, 45071 Orléans, France*
[2]*LEMA CNRS, UMR 6157, IUT de Blois, 3 place Jean Jaurès, 41029 Blois, France*
[3]*EM2C CNRS, UPR 288, Ecole Centrale Paris, Grande Voie des Vignes, 92295 Châtenay-Malabry, France*
[4]*CIRIMAT CNRS, UMR 5085, Université Paul Sabatier, 118 Route de Narbonne, 31062 Toulouse, France*

A multiscale numerical model is developed to predict the thermal radiative properties (TRP) of rough $La_2NiO_{4+\delta}$ coatings. The model integrates intrinsic and extrinsic contributions related to the chemical composition and the texture, respectively. High-temperature infrared reflectivity and thermogravimetric measurements on a $La_2NiO_{4+\delta}$ single crystal make it possible to understand the role of the excess oxygen in the intrinsic TRP. We show that dense ceramics with thicknesses higher than 4 μm are optically thick, and that one can adjust the surface roughness parameters to predict their TRP.

Solid oxide fuel cells (SOFCs) with a planar configuration are of great interest as efficient and ecologically clean energy conversion systems. At the highest operating temperatures ($T \sim 1000$ K), thermal gradients inside the cell and at the contacts lead to mechanical failures that limit the usefulness of the devices.

However, for engineers aiming to suppress this unwanted behavior, only a few thermophysical parameters (phonon thermal conductivity, radiative conductivity) that are required to predict the temperature field at the operating temperature are available in the literature. Moreover, since the ceramics used in SOFCs are often heterogeneous, the knowledge of their thermophysical properties is not straightforward. In particular, the thermal radiative properties (TRP) of SOFCs ceramic are unknown and, in more general viewpoint, few attempts have been made to establish a firm connection between the textural parameters and TRP.[1] To solve this issue, we develop a numerical methodology integrating material parameters (chemical and textural) from the nanometer scale to the millimeter scale.

$La_2NiO_{4+\delta}$ is used in SOFCs due to its favorable ionic and electronic properties.[2] Thus, in this compound, the oxygen over-stoichiometry (δ) plays a crucial role in its structural properties,[3] since it relaxes the constraints of the distorted undoped compound and creates holes in the NiO_2 planes, inducing highly anisotropic behavior.[4] Understanding the role of δ as a function of temperature, is therefore, necessary to predict the intrinsic TRP, as has been shown by some of the authors for the isostructural $Pr_2NiO_{4+\delta}$ system.[5]

In this paper, we report high-temperature infrared reflectivity measurements on a $La_2NiO_{4+\delta(T)}$ single crystal and correlate them with the temperature dependence of δ. We then use a numerical tool based on a Monte Carlo ray-tracing (MCRT) code[6] aiming to predict the contribution played by the surface roughness of model rough dense ceramics of $La_2NiO_{4+\delta}$.

a)Electronic mail: benoit.rousseau@cnrs-orleans.fr.

The crystals were grown in air by the floating zone technique in an image furnace (Cyberstar). The feed rod was sintered in air at 1300 °C for 12 h and prepared from $La_2NiO_{4.18}$ powders according to the Pecchini method.[7] The chemical composition was checked by Inductively Coupled Plasma spectrometry for cationic composition, and thermogravimetric analysis—differential scanning calorimetry (TGA-DSC) and iodometric titration for oxygen content. The crystallinity and the structure of the crystal were checked by Laue and powder x-ray diffraction (XRD) on a single crystal and a ground crystal, respectively. Infrared reflectivity spectra ($\rho(\omega)$) were measured over the range 300–1000 K with a Fourier Transform Infrared (Bruker 113v) spectrometer with the electric field lying in the *ab* plane and along the *c* axis.[8,9]

Figure 1 presents the XRD pattern of the ground crystal. Rietveld analysis with the space group $I4/mmm$ shows that the sample is single-phase and consistent with the tetragonal K_2NiF_4 type structure. Chemical analyses lead to a $La_2NiO_{4.11}$ composition for the single crystal. In order to determine the evolution of δ, TGA-DSC measurements were performed on the ground crystal under the same temperature conditions as in the spectrometer (inset in Fig. 1). We ob-

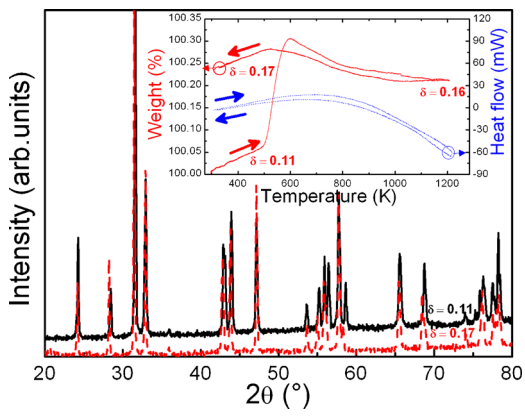

FIG. 1. (Color online) Room temperature XRD patterns of $La_2NiO_{4+\delta}$ crushed single crystal (δ=0.11 and 0.17) and Inset: TGA-DSC measurements under air for $La_2NiO_{4+\delta}$ crushed single crystal.

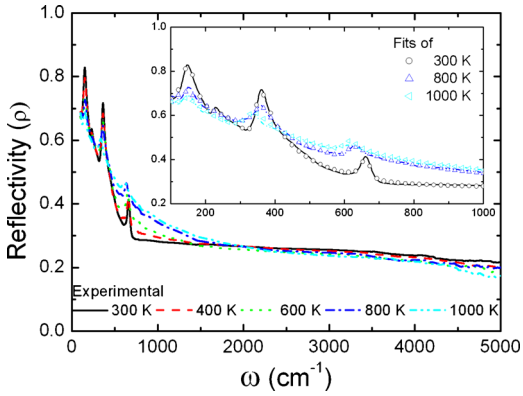

FIG. 2. (Color online) Measured infrared reflectivity of a $La_2NiO_{4.11}$ single crystal for the electric field lying in the *ab* plane at various temperatures. The inset shows fits (symbols) to the experimental reflectivity spectra (solid lines) at 300, 800, and 1000 K in the spectral range up to 1000 cm^{-1}.

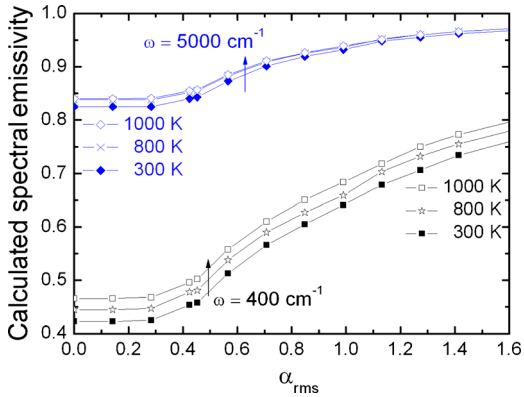

FIG. 3. (Color online) Calculated spectral emissivity of a $La_2NiO_{4+\delta}$ single crystal as a function of surface roughness characterized by the standard deviation of the slopes α_{rms} at two frequencies (ω) and three temperatures. Fixing the rms height-ω_{rms} at 7.68 μm, and varying the correlation length-τ. The length of the samples is 511.5 μm; with a resolution of 0.5 μm. The standard deviation (0.04%) gives a good precision with a fast simulation speed.

serve an abrupt weight gain at about 320 K and at above 620 K, the sample begins to lose the oxygen and continues losing it up to 1200 K. The weight gain with heating shows that δ increases ($\delta_{after}=0.17$ compared to $\delta_{before}=0.11$), and that re-oxidation occurs. Note that at 1000 K, $\delta\sim0.16$, so the electronic concentration remains sufficiently high to generate efficient optical absorption.[5] Moreover, no peak is observed in the DSC curve, showing that there is no decomposition or structural transition during the temperature cycle. This was confirmed by XRD on the final product as shown in Fig. 1.

The reflectivity spectra $\rho(\omega)$ in the *ab* plane, (Fig. 2) exhibits two remarkable microscopic mechanisms: (i) infrared-active phonons in which mobile polarons are superimposed[8] (wavenumber $\omega<1000$ cm^{-1}), and (ii) trapped polarons resulting from the coupling between the charge carriers induced by the chemical doping and the lattice ($\omega>1000$ cm^{-1}). To obtain the complex refractive index of the La_2NiO_4 single crystal, we model $\rho(\omega)$ with the double-damping Drude (DDD) dielectric function ($\tilde{\varepsilon}$).[9–11] This function takes into account the contributions of the phonons and of the trapped carriers and an extended Drude term is added to describe the response of the mobile carriers. The advantages and limitation of this model have been intensively discussed with respect to other models in the literature.[5,11] Some of the modeled spectra are shown in Fig. 2 and the fitting procedure is consistent with previous works.[10,12] Due to the re-oxidation, the level and shape of each $\rho(\omega)$ are not greatly affected by the temperature increase. This suggests that optical mechanisms involving the trapped and mobile carriers are active at high temperatures, consistent with the TGA results (inset of Fig. 1). In fact the study of the optical behavior of the single crystal make it possible to model the optical response imposed by the carriers in the *ab* plane. Then, the good agreement (inset in Fig. 2) between the experimental and fitted spectra ensures that the optical parameters are reliable.

The index of refraction (n) and extinction coefficient (k) can be derived as $n=\mathrm{Re}(\sqrt{\tilde{\varepsilon}})$ and $k=\mathrm{Im}(\sqrt{\tilde{\varepsilon}})$, respectively. With these values, we can calculate the TRP of model dense and rough ceramics composed of randomly oriented submicron grains, by averaging[13] the complex dielectric functions in the *ab* plane and along the *c* axis. n and k can then be introduced into a homemade MCRT code[6] to obtain the TRP.

By considering that a ceramic is opaque if $Kd>1$, where d is the thickness of the layer and $K=4\pi k\omega$ is the absorption coefficient, we checked that a dense ceramic of $La_2NiO_{4+\delta}$ is opaque for a minimum thickness of 3.67 μm over the entire measured temperature range (3.67 μm, 2.77 μm, and 2.35 μm for 300 K, 800 K, and 1000 K, respectively).

Since for a real coating the surface is often rough, we integrate this contribution in our model. To quantify this effect[14] on the TRP, we have made calculations for a Gaussian rough surface (GRS) with a roughness slope ($\alpha_{rms}=\sqrt{2}(\omega_{rms}/\tau)$) varying from 0 to 2. MCRT code[6] calculations were performed with 10^4 photon rays for three-dimensional surfaces with different slopes. The optical indices (n,k) at two frequencies and three temperatures (400 and 5000 cm^{-1} at 300, 800, and 1000 K) were used to calculate the variation in normal spectral emissivity with surface roughness (Fig. 3). The shapes of the three curves are very similar to those obtained by other authors[15] for metallic rough coatings. In particular, the results show that the emissivity increases with roughness when the slope of the GRS is greater than 0.28. Note that for a real cathodic layer composed of $La_2NiO_{4+\delta}$,[6] α_{rms} is smaller than 0.28. It confirms our prediction that in this case the emissivity is not influenced by the roughness. On the other hand, for a GRS of $Pr_2NiO_{4+\delta}$. ($Pr_2NiO_{4+\delta}$ is isostructural to $La_2NiO_{4+\delta}$) with higher slope ($\alpha_{rms}=0.64$), a previous work has shown experiments verify a similar theoretical curve.[16]

In summary, the thermal radiative properties of $La_2NiO_{4+\delta}$ single crystal were investigated to study their temperature evolution at different values of the δ. By using a DDD model, the complex index of refraction was extracted from the reflectivity spectra acquired by infrared spectroscopy at high temperature. These results were introduced into a multiscale numerical model aiming to predict the TRP of cathodic layers on SOFCs as a function of surface roughness. This work shows how we can modify the TRP of an opaque rough coating by adjusting its chemical and textural parameters.

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