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Temperature-dependent infrared properties of Ca doped (La,Sr)MnO_3 compositions with potential thermal control application

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HIGHLIGHTS

► Infrared properties of Ca doped (La,Sr)MnO_3 compositions are investigated.
► These compositions exhibit a tunable infrared properties basing on their temperature.
► The potential application of the compositions in thermal management is discussed.

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ABSTRACT

The synthesized compositions $La_{0.7}Ca_{0.3-x}Sr_xMnO_3$ show their potential in thermal control application. The crystal structure, surface morphology, and the temperature dependence of resistivity, infrared spectra and emissivities for the compositions are reported. All of the synthesized compositions exhibit the characteristics of perovskite structure and of metal–insulator transition. Crystal structure of the compositions changes from the orthorhombic to the rhombohedral structure with increasing doping level (x). The infrared properties of compositions can be automatically adjusted basing on variation in temperature. In the temperature range 97–373 K, the variation amplitude of infrared emissivity exceeds 0.5. The potential application of the compositions in thermal management is discussed.

1. Introduction

Spacecraft in orbit are subjected to space environment temperature fluctuation. In order to maintain all the component of spacecraft within their respective temperature range, an efficient thermal control system is necessary [1]. Thermal control coating is one of the popular materials to be used in the thermal control system. It can achieve a temperature balance in spacecraft by adjusting its thermal infrared properties, such as spectral reflectivity and emissivity, which determine the heat rejection of spacecraft. Since traditional thermal control coating has fixed thermal infrared reflectivity and emissivity, such as OSR and Aluminum, it requires a large and complex temperature control system to adjust the heat rejection in response to temperature fluctuation. This inevitably increases the costing and bulkiness of thermal control system. One expected solution is to develop an advanced thermal control material that can adjust its thermal infrared properties automatically in response to variation in temperature without additional power consumption and moving parts.

Perovskite-type manganese oxides doped with alkaline-earth elements display such properties [2–4]. Recent studies showed their potentiality for thermochromic devices due to their metal–insulator (MI) transitions. For example, in the vicinity of $x = 0.2$, manganese oxides $La_{1-x}Sr_xMnO_3$ showed remarkable emissivity increase upon heating [4–7]. In addition, J. Huang et al. [8] theoretically investigated the thermal radiative properties of structured material $La_{0.825}Sr_{0.175}MnO_3$ combined with Al and SiO_2 gratings and their research indicated that emissivity increment is enhanced in the entire calculated temperature range for the structured surface. These investigations mainly focused on manganese oxides (La,Sr)MnO_3, especially Sr doping level $x = 0.175$. For the manganese oxides $La_{0.825}Sr_{0.175}MnO_3$, it exhibit abrupt metal–insulator transition at $T_{MI} = 283$ K [4]. Though such composition could be a potential candidate for thermal control material, the T_{MI} remain low for applications. The $La_{0.7}Ca_{0.3-x}Sr_xMnO_3$ (LCSMO) is also interesting especially for the Ca rich composition. The magnetoresistance effect behavior of this composition has been already studied in Ref. [9]. The LCSMO compositions also exhibit a low emissivity below the transition temperature T_{MI} and a high emissivity above T_{MI}. The T_{MI} can be adjusted close to room temperature by appropriate Ca:Sr ratio. If the material is coated to the surface of

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spacecraft, it can adjust the surface temperature by changing its emissivity. With this mechanism, our study is motivated to provide additional knowledge on the properties of manganese oxides.

In this work, the characteristics of resistivity, infrared emissivity, and spectral reflectivity for the $La_{0.7}Ca_{0.3-x}Sr_xMnO_3$ ($x = 0.1$, 0.12, 0.135, and 0.15) compositions at various temperature are investigated. For further comparison, these characteristics of $La_{0.825}Sr_{0.175}MnO_3$ (LSMO) are presented as well.

2. Experiment

A series of samples $La_{0.7}Ca_{0.3-x}Sr_xMnO_3$ ($x = 0.1$, 0.12, 0.135, and 0.15) and $La_{0.825}Sr_{0.175}MnO_3$ are synthesized by a conventional solid–state reaction method at high temperature. The La_2O_3, $CaCO_3$, $SrCO_3$, and MnO_2 (99.99% purity) powders are used as raw materials during the solid-state reaction processing. The powder of La_2O_3 is pre-heated at 1273 K for 8 h before weighed. The other raw materials are also dried at 423 K for 4 h to remove the moisture content. These raw materials are ground for 8 h with the ethanol. After dried, the powder mixtures are fired repeatedly in the muffle furnace for 20 h at 1273 K. The resultant powders are pressed into pellets 40 mm in diameter and 4 mm thick. The pellets are then sintered for 22 h in air at temperatures 1723 K. After cooled to room temperature, the as-prepared pellets are annealed in a flowing oxygen atmosphere of 20 ml/min at 1273 K for 10 h. Finally, the test samples are machined and polished into discs with 25 mm in diameter and 0.4 mm thick.

The structure of samples is characterized by X-ray diffraction (XRD, D8 ADVANCE, Bruker Co., Germany) with Cu-Kα radiation at room temperature. Microstructure of samples is analyzed by field-emission scanning electron microscopy (SEM, S-4800, Hitachi Co., Japan) before polished. The root-mean-square (RMS) roughness of the polished samples is detected by atomic force microscopy (AFM, CSPM4000, Being Ltd., China). The electrical resistivity of the samples, as a function of temperature, is measured with a physical property measurement system (PPMS-14, Quantum Design Co., America) from 150 K to 350 K using the standard four probe ac method. The accessory of Transmission-Reflection Dewar (Catalog No. DER-300, Harrick Scientific Products, Inc., America) is mounted directly in the FT-IR spectrometer (VERTEX80v, Bruker Co., Germany) to measure the temperature-dependent infrared spectra (15° incident angles, 16 scans, resolution 2 cm^{-1}) of all samples over the range from 4000 to 400 cm^{-1}. Temperature of these samples from 97 K to 373 K is controlled using liquid nitrogen and two heating cartridges. A gold film is employed as a reference mirrors to determine the reflectivity.

3. Measuring methods of emissivity

Generally, there are three methods to measure the emissivity, i.e. direct measurement, indirect measurement from the reflectivity spectra and calorimetric measurement [10–12]. For opaque manganese oxides, indirect measurement is a good alternative to determine the emissivity because a reflectivity measurement is currently performed. From a radiation balance on a certain medium, the flux of radiation can be expressed as follows

$$\rho_\lambda + \alpha_\lambda + \tau_\lambda = 1, \qquad (1)$$

where ρ_λ, α_λ, and τ_λ is the spectral reflectivity, the spectral absorptivity, and the spectral transmissivity of the flow respectively. For an opaque materials, there is no transmission, and the absorption and reflection are surface processes for which $\rho_\lambda + \alpha_\lambda = 1$. According to Kirchoff's law, the spectral emissivity ε_λ can be deduced from spectral reflectivity. It follows that $\alpha_\lambda = 1 - \rho_\lambda = \varepsilon_\lambda$.

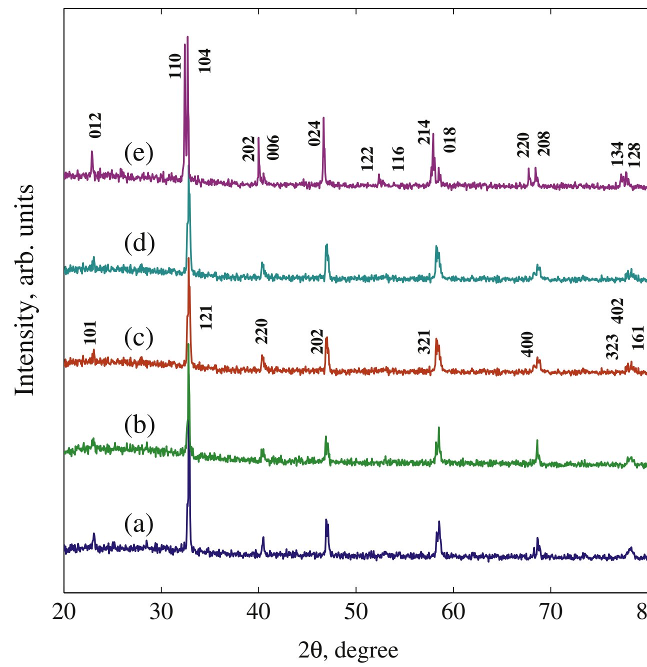

Fig. 1. XRD patterns of (a) $La_{0.7}Ca_{0.2}Sr_{0.1}MnO_3$, (b) $La_{0.7}Ca_{0.18}Sr_{0.2}MnO_3$, (c) $La_{0.7}Ca_{0.165}Sr_{0.135}MnO_3$, (d) $La_{0.7}Ca_{0.15}Sr_{0.15}MnO_3$, and (e) $La_{0.825}Sr_{0.175}MnO_3$.

For a sample with the temperature-dependent infrared reflectivity spectra, its infrared emissivity can be obtained by integrating the spectral reflectivity in the wavelength range from 2.5 μm (4000 cm^{-1}) to 25 μm (400 cm^{-1}) as follows:

$$\varepsilon(T) = \frac{\int_{2.5}^{25} [1 - \rho(\lambda, T)] E_{\lambda,b}(\lambda, T) \mathrm{d}\lambda}{\int_{2.5}^{25} E_{\lambda,b}(\lambda, T) \mathrm{d}\lambda}. \qquad (2)$$

Where $E_{\lambda,b}(\lambda, T) = C_1 \lambda^{-5} [\exp(C_2/\lambda T) - 1]^{-1}$, the value of first and second radiation constants is $C_1 = 3.742 \times 10^8$ W $\mu m^4/m^2$ and $C_2 = 1.439 \times 10^4$ mK, respectively.

In this work, the temperature-dependent reflectivity spectra $\rho(\lambda,T)$ are measured by experiment. In the temperature range of 97–373 K, we take 89% of the radiant energy of blackbody at 373 K with wavelengths between 2.5 μm and 25 μm into account.

4. Results and discussions

The structure of all samples is characterized by powder XRD at room temperature. The XRD patterns (in Fig. 1) show that all the samples are single phase, and exhibit the characteristic peaks of the perovskite structure. Table 1 lists the structure parameters and the

Table 1
Structure parameters and metal–insulator transition temperature for the samples.

Sample	Space group	Lattice parameters (Å)			T_{MI} (K)
		a	*b*	*c*	
$La_{0.7}Ca_{0.2}Sr_{0.1}MnO_3$	*Pnma*	5.4489	7.7209	5.4932	251
$La_{0.7}Ca_{0.18}Sr_{0.12}MnO_3$	*Pnma*	5.4477	7.6931	5.501	270
$La_{0.7}Ca_{0.165}Sr_{0.135}MnO_3$	*Pnma*	5.4566	7.7171	5.5024	295
$La_{0.7}Ca_{0.15}Sr_{0.15}MnO_3$	$R\bar{3}c$	5.4719	–	13.3198	301
$La_{0.825}Sr_{0.175}MnO_3$	$R\bar{3}c$	5.527	–	13.3452	281