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Investigation into the Composition, Structure and Properties of $La_{(1-x)}Sr_xMnO_3$ Powders Obtained via Solid-State Synthesis

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Abstract—The results of collaborative research into the phase and grain-size compositions, diffuse reflection spectra, and the temperature-dependent emissivity of $La_{(1-x)}Sr_xMnO_3$ compounds synthesized as powders from $La_2O_3 + SrCO_3 + MnCO_3$ mixtures, performed for the first time at temperatures from –70 to +120°C, are presented. It is demonstrated that they can be used in creating smart coatings in the form of paints to stabilize the temperature of objects.

Keywords: phase transitions, powders, emissivity, temperature stabilization, rare-earth manganites
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INTRODUCTION

At a specific concentration of strontium substitutional atoms in $La_{(1-x)}Sr_xMnO_3$ compounds, the Curie point can be shifted from the negative to positive region, i.e., to room temperature and higher [1]. This property has practical applications. In the range from –100 to +120°C, the temperature dependences of the emissivity of $La_{(1-x)}Sr_xMnO_3$ ceramic plates, $\varepsilon = f(T)$, were first investigated in [2] with the aim of preparing coatings capable of stabilizing the temperature of objects, namely, thermal stabilizing coatings (TSCs). Such investigations were also continued with the help of ceramic plates [3, 4]. However, ceramic plates are not easily producible especially if a complicated configuration is deposited onto their surface and can exfoliate during operation. These drawbacks can be eliminated by creating TSCs in the form of paints.

It is advisable that the pigment of these paints be synthesized in the form of powders, rather than by the grinding of ceramics, because mechanical action substantially increases the concentration of intrinsic defects. Under operating conditions, these defects upon irradiation transform into color centers, leading to changes in the optical properties [5, 6].

The synthesis temperature must be lower than the sintering temperature of the powders ($T = 1300$°C for $La_{(1-x)}Sr_xMnO_3$). Hence, it is necessary to develop powder synthesis technologies: TSC pigments, which must provide a high yield of the main phase. The powders should possess the required characteristics of phase transitions in the dependences $\varepsilon = f(T)$, diffuse reflection spectra ρ_λ in the solar-radiation region, and high values of photostability and radiation resistance.

The goal of this work is to study the possibilities of the solid-state synthesis of $La_{(1-x)}Sr_xMnO_3$ powders with operating characteristics (quantity $\varepsilon = f(T)$ and spectrum ρ_λ) corresponding to "smart"-coating pigments.

EXPERIMENTAL

La_2O_3, $MnCO_3$, and $SrCO_3$ powders with the purity grades OSCh and KhCh were mixed in the necessary weight ratios and diluted with distilled water. The mixture was dispersed using a magnetic stirrer over 2 h, evaporated at $T = 150$°C, and heated in the mode 800°C × 2 h → 1200°C × 2 h, which is more efficient than one-time heating [5].

The powder-particle size distribution functions were calculated via the linear-intercept method according to images obtained by means of a TM-1000 scanning electron microscope. X-ray phase analysis was performed using a Shimadzu XRD-6000 diffractometer. The spectra ρ_λ were recorded by means of a Perkin Elmer Lambda 950 spectrophotometer in the range of 0.2–2.8 μm. The dependences $\varepsilon = f(T)$ were recorded via the calorimetric method with the use of a Term setup. Measurements were carried out in vacuum (10^{-6} Torr) at temperatures varying from –70 to +120°C [5].

EXPERIMENTAL RESULTS AND DISCUSSION

Under the conditions of twice heating, synthesis stimulates the formation of powders with three types of particle sizes: 0.92, 1.94, and 2.32 μm. The first of them corresponds to grains (single crystallites); the

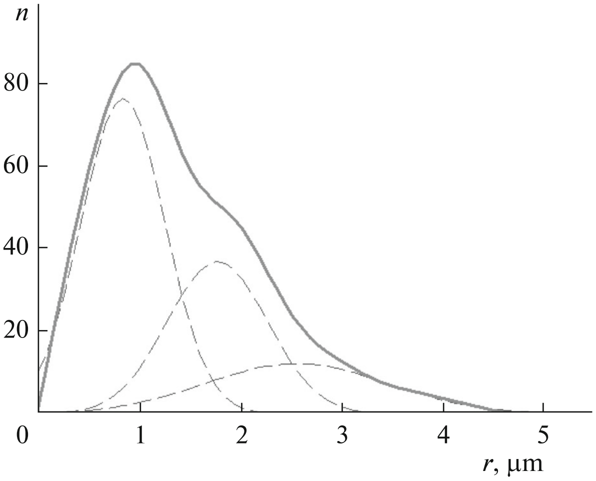

Fig. 1. Powder-particle size distribution function and its expansion into Gaussians.

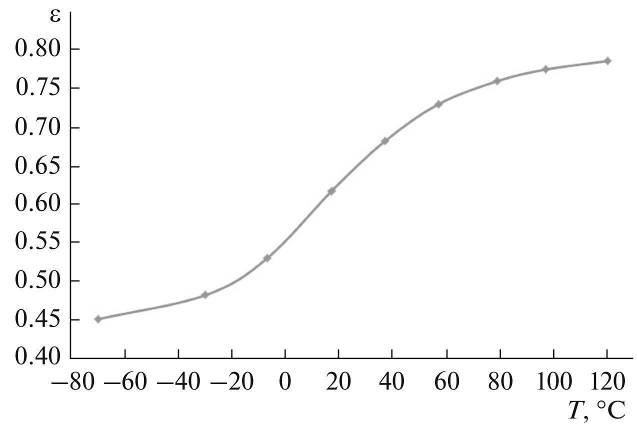

Fig. 2. Dependence between the emissivity and the temperature of the powder containing 92.3% of $La_{0.825}Sr_{0.175}MnO_3$ and 7.7% of Mn_3O_4.

second, to granules composed of these grains; and the third, to granules incorporating the aforementioned and smaller (0.5 μm) grains [5].

X-ray phase analysis demonstrated (Fig. 1) that the synthesized powder comprises $La_{0.825}Sr_{0.175}MnO_3$ (92.3 wt %) and Mn_3O_4 (7.7 wt %). In the temperature range under study, the powder emissivity (Fig. 2) varies from 0.79 (ε_{max}) to 0.45 (ε_{min}). Their difference ($\Delta\varepsilon$) is 0.34. Comparison with the values inherent to the $La_{(1-x)}Sr_xMnO_3$ ceramic samples (namely, ε_{max} = 0.737 and $\Delta\varepsilon = 0.371$ [3]) indicates their insignificant discrepancy. In the case of the experimental dependence $\varepsilon = f(T)$ of the powder consisting entirely of $La_{(1-x)}Sr_xMnO_3$, calculations performed with allowance for the characteristics of Mn_3O_4 ($\varepsilon = 0.9$, $\varepsilon \neq f(T)$, and $C = 7.7\%$) demonstrate that the obtained data better approximate the values typical of the ceramic samples.

For the range of 0.2–2.5 μm, a "dip" corresponding to 500–650 nm is recorded in the spectrum ρ_λ of the powder under consideration. In this case, the minimum reflection coefficient is observed at a wavelength of 620 nm. This dip is caused by an absorption band with the same maximum. Such a band was earlier recorded in the absorption spectra of $La_{(1-x)}Sr_xMnO_3$ compounds [6–10] and attributed to the existence of two (paramagnetic and ferromagnetic) phases.

When the wavelength increases, the reflection coefficient is recorded in the near-IR region. Calculations based on the Kubelka–Munk–Gurevich formula indicate that, in this region, the absorption coefficient k decreases with increasing wavelength according to the power law: $k = \alpha\lambda^\beta$. Such a dependence with the positive exponent β is characteristic of the free-electron energy distribution in the conduction band of semiconductors [11]. In the given case, the exponent is negative. This provides the inverse free-electron energy distribution and signifies the substantial contribution of the ferromagnetic component to this distribution.

Thus, the performed investigations demonstrated that, in the twice heating mode 800°C × 2 h → 1200°C × 2 h, solid-state synthesis from the $LaO_3 + MnO_2 + SrCO_3$ powder mixture makes it possible to obtain the $La_{(1-x)}Sr_xMnO_3$ powder whose concentration is 92.3%. The synthesized powder includes 0.92-μm grains and 1.94- and 2.32-μm granules. Powder-particle sizes fall within the solar-spectrum wavelength range, assuming their influence on scattering and diffuse reflection. The powder emissivity varies from 0.45 to 0.79; i.e., its values coincide closely with the ranges calculated using ceramic plates [2, 3, 7]. The behavior

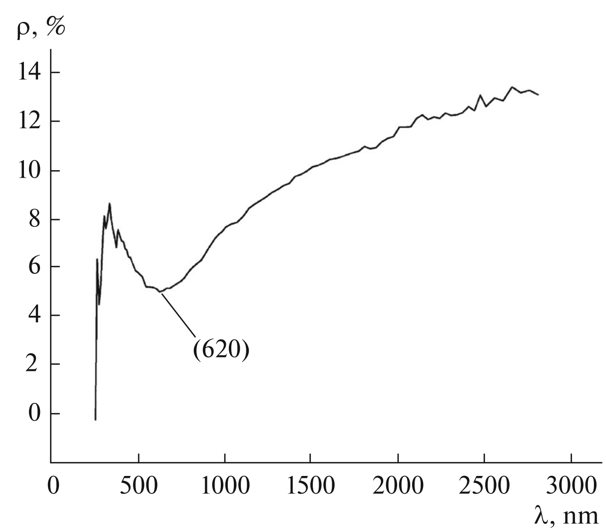

Fig. 3. Diffuse-reflection spectrum of the powder composed of the $La_{0.825}Sr_{0.175}MnO_3$ compound (92.3%) and Mn_3O_4 manganese oxide (7.7%).

of the dependence $\varepsilon = f(T)$ is evidence that the synthesized powder incorporates ferromagnetic and paramagnetic phases. This is also confirmed by the diffuse-reflection spectrum characterized by an absorption band in the visible region and the power law of the reflection coefficient in the near-IR region (the latter is determined by the simultaneous existence of the aforementioned two phases).

CONCLUSIONS

The results of the study demonstrated that solid-state synthesis provides the possibility of creating $La_{(1-x)}Sr_xMnO_3$ powders whose phase and grain-size compositions, diffuse-reflection spectra, and temperature-dependent emissivity correspond to the characteristics of the pigments of smart thermal stabilizing coatings.

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