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Thermal and magnetocaloric properties of manganites $La_{0.7}Sr_{0.3-x}Ba_xMnO_3$

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The results of a study of the effect of partial substitution of Sr^{2+} ions by Ba^{2+} ions on the thermophysical and magnetocaloric properties of manganite $La_{0.7}Sr_{0.3-x}Ba_xMnO_3$ ($x = 0$; 0.02; 0.05 and 0.10) in the temperature range 100−400 K and in a magnetic field up to 1.8 T. It is shown that such a substitution leads to a significant decrease in T_C. In the behaviour of the thermal diffusivity $\eta(T)$ and thermal conductivity $\kappa(T)$ near T_C, minima were found that are associated with both the scattering of phonons by local distortions of the crystal lattice and by spin fluctuations. The absolute values of thermal conductivity decrease with an increase in the disorder parameter. The magnetocaloric effect exhibits a weak dependence on the substitution level (x).

Keywords: Magnetocaloric effect, manganites, phase transitions, heat capacity, thermal diffusivity, thermal conductivity.

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1. Introduction

Doped manganites ($Re_{1-x}A_xMnO_3$, where Re — rare earth element, A — alkaline-earth metal), widely known due to the effect discovered in them of colossal magnetoresistance [1,2] still remain in the field of view of researchers, among other things, because of the observed magnetocaloric effect in them, which is comparable in magnitude to the effect in the best magnetocaloric materials [3,4]. The magnetocaloric effect is of interest as a basis for the creation of magnetic cooling technology, which has recently obtained considerable attention [4]. In addition, manganites are model objects for studying the fundamental properties of strongly correlated electronic systems.

The properties of manganites are mainly determined by the ratio of the number of different-valence ions Mn^{3+}/Mn^{4+}, and an important role in the behavior of thermophysical properties is played by such microscopic parameters as local distortions of the crystal lattice, characterized by the disorder parameter $\sigma^2 = \Sigma x_i r_i^2 - \langle r_A^2 \rangle$ caused by distinguishable in ionic radii and average value of ionic radii A-cations $\langle r_A \rangle = 0.7r_{La} + (0.3-x)r_{Sr} + xr_{Ba}$, where r_{La}, r_{Sr} and r_{Ba} are the radii of the La, Sr, and Ba ions, respectively.

The correlation between σ^2 and $\langle r_A \rangle$ changes and thermophysical properties was found in the study of $Pr_{0.7}Sr_{0.3-x}Ca_xMnO_3$ manganite [5,6]. In addition, it has been shown that partial substitution in both the A sublattice and the Mn sublattice can be used to improve the magnetocaloric properties [5–7]. In this composition, the Sr^{2+} ion is replaced by an ion of smaller radius Ca^{2+}, which creates „chemical pressure“, which leads to deformation (compression) of the crystal lattice and a decrease as σ^2 and $\langle r_A \rangle$. The consequence of this substitution is the weakening of exchange interactions and, as a consequence, a decrease in T_C. In this work, the opposite situation is considered: an ion of smaller radius Sr^{2+} is replaced by an ion of larger radius Ba^{2+}, which should lead to expansion of the crystal lattice and corresponding changes in the values of σ^2, and $\langle r_A \rangle$. In calculations, we took the values of ionic radii corresponding to the value of the coordination number 8: $r_{La} = 1.18$ Å, $r_{Sr} = 1.26$ Å, $r_{Ba} = 1.42$ Å [8].

This work presents the results of an experimental study of the effect of partial substitution of Sr for Ba on the heat capacity, thermal conductivity, thermal diffusivity, and magnetocaloric effect in the $La_{0.7}Sr_{0.3-x}Ba_xMnO_3$ ($x = 0$; 0.02; 0.05 and 0.10) in the temperature range of 100−400 K and in magnetic fields up to 1.8 T.

2. Specimens and experiment

The samples were manufactured using standard ceramic technology [9]. The heat capacity and thermal diffusivity were measured by ac-calorimetry and these data were used to determine the thermal conductivity, which are related by the relation $\kappa = \frac{d}{M} C_P \eta$, where d — sample density, M — its molar mass, C_P — heat capacity, η — thermal diffusivity, κ — thermal conductivity. Direct measurements of the adiabatic temperature change ΔT_{ad} with a change in the magnetic field were carried out by the modulation method [10]. The principle of the method is that an

alternating magnetic field is applied to the sample, which, due to the magnetocaloric effect, induces a periodic change in the temperature of the sample. This change in the temperature is recorded by a synchronous detector by means of a differential thermocouple, one junction of which is glued to the test sample, the other — to the copper block. The frequency of variation of the alternating magnetic field in this experiment was 0.2 Hz. This technique allows to register temperature changes with an accuracy no worse than 10^{-3} K. A variable magnetic field with a strength of 1.8 T was created by a magnetic field source manufactured by Agency for International Trade Information and Cooperation. Copper-constantan and chromel-constantan thermocouples were used as thermal sensors.

3. Results and discussions

To establish the relationship between the physical properties and the microscopic parameters σ^2 and $\langle r_A \rangle$, the values of the latter were calculated depending on x, which are given in the table, the Curie temperature was determined from the maximum of the heat capacity anomaly.

The table shows that substitution of an ion of smaller radius (Sr) by an ion of larger radius (Ba) leads to an increase in the average ionic radius $\langle r_A \rangle$ and the disorder parameter σ^2. It should be noted that $\langle r_A \rangle$ and σ^2 have different effects on the magnetic and thermophysical properties of manganite. An increase in the average ionic radius is accompanied by an increase in the angle Mn−O−Mn, which leads to an increase of T_C — this means an increase in the intensity of exchange interactions. Meanwhile, the distortion of the crystal lattice caused by the spread in the ionic radii of A-cations, which are associated with σ^2, in this case causes an increase in the volume of the unit cell and lengthening of the Mn−O bonds [11–13], which should lead to a weakening of exchange interactions and a decrease in T_C. In general, when both $\langle r_A \rangle$ and σ^2 change during substitution, the dependence $T_C = f(\langle r_A \rangle, \sigma^2)$ has a complex character. It can be assumed that the observed decrease in the value of T_C with increasing x is due to the predominance of the influence of the disorder parameter σ^2 over the increase in the average ionic radius.

Let us consider in more detail how such a substitution affects the behavior of such macroscopic parameters as heat capacity, thermal diffusivity, thermal conductivity, and the magnetocaloric effect. Figure 1 shows the results

Some system parameters $La_{0.7}Sr_{0.3-x}Ba_xMnO_3$

x	T_C, K	$\langle r_A \rangle$, Å	σ^2, Å^2
0	362	1.2040	$1.2 \cdot 10^{-3}$
0.02	343	1.2072	$2.1 \cdot 10^{-3}$
0.05	324	1.2120	$2.9 \cdot 10^{-3}$
0.10	280	1.2200	$5.3 \cdot 10^{-3}$

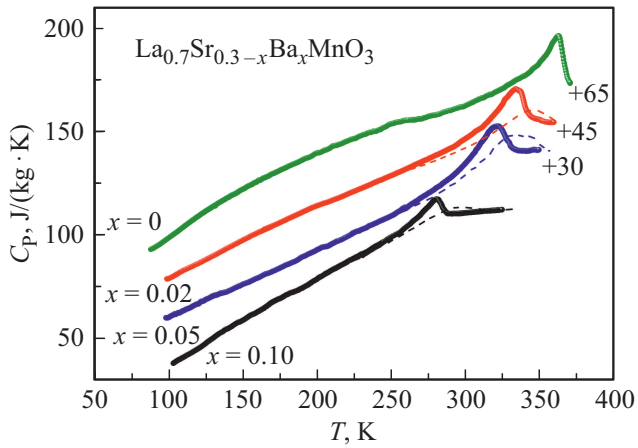

Figure 1. Temperature dependence of heat capacity for $La_{0.7}Sr_{0.3-x}Ba_xMnO_3$ at $H = 0$ (points) and at $H = 1.8$ T (dashed lines). For clarity, the curves C_P are shifted by the indicated units C_P.

of measuring the temperature dependence of the heat capacity for the $La_{0.7}Sr_{0.3-x}Ba_xMnO_3$ system at $H = 0$ and $H = 1.8$ T. For all samples, pronounced anomalies associated with the ferromagnet-paramagnet (FM−PM) phase transition are observed, with a maximum at temperatures $T_C = 362$, 343, 324 and 280 K for $x = 0$, 0.02, 0.05 and 0.1, respectively. As we can see from the figure, the magnetic field suppresses the anomalies and shifts the temperature of the maximum towards higher temperatures. An increase in the Ba concentration leads to a T_C shift towards lower temperatures. This is due to a decrease in the exchange interaction between manganese ions due to an increase in the distance between magnetically active atoms when strontium ions are replaced by barium ions with a large ionic radius.

The temperature dependences of the abnormal part of the heat capacity and the change in the entropy of the phase transition at $H = 0$ were obtained from the heat capacity data, they are shown in Fig. 2, *a* and *b*. The abnormal part of the heat capacity was defined as $\Delta C_P(T) = C_P - C_{ph}$, where C_{ph} is the lattice contribution obtained by extrapolating the Debye heat capacity curve, C_P is the measured value of heat capacity. As can be seen from Fig. 2, *a*, the maximum value of the heat capacity jump in the phase transition area is $\Delta C_P \approx 28$ J/mol · K for sample with $x = 0$ and the minimum value $\Delta C_P \approx 12$ J/mol · K is observed for the sample with $x = 0.1$, i.e. with growth the replacement value of the jump ΔC_P decreases significantly.

Figure 2, *b* shows the temperature dependences of the entropy change associated with the disordering of the magnetic system during the ferromagnet-paramagnet phase transition, which were determined by the formula: $\Delta S^*(T) = \int(\Delta C_P/T)dT$. The ΔS^* values for the $La_{0.7}Sr_{0.3-x}Ba_xMnO_3$ system vary from 1.20 to 2.38 J/K, which is much less ideal values for the Ising model ($\Delta S^* = R \ln 2 = 5.7$ J/K) and Heisenberg model

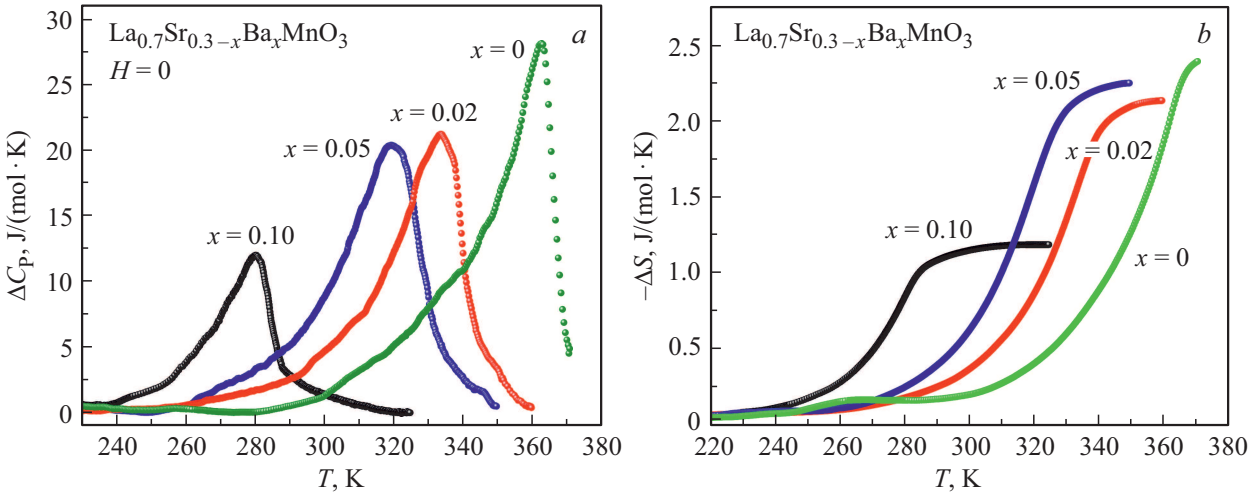

Figure 2. *a*) Temperature dependence of the abnormal part of the heat capacity (*a*) and the change in the phase transition entropy at $H = 0$ (*b*).

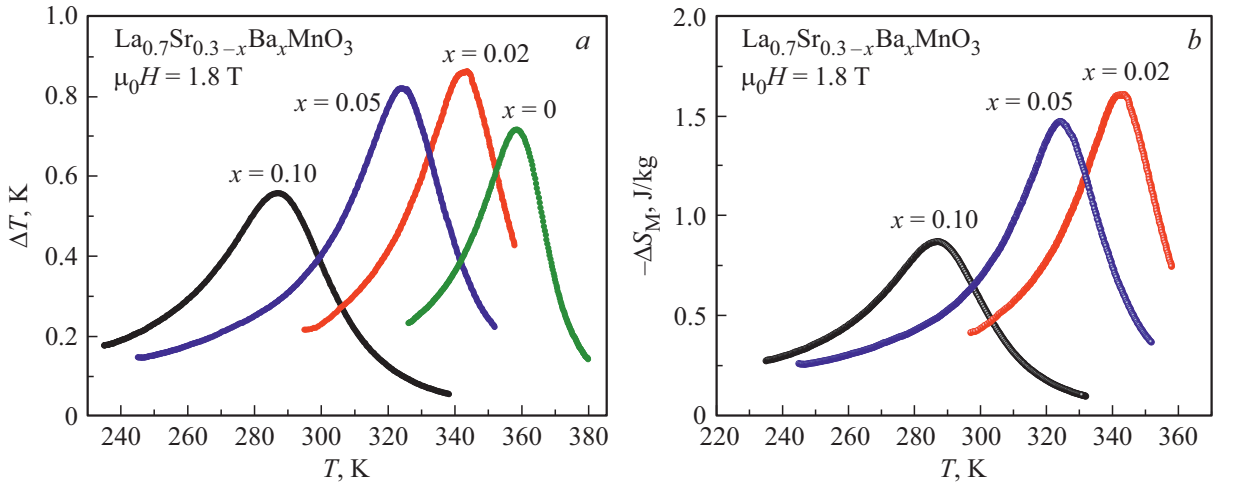

Figure 3. Temperature dependence of the MCE (*a*) and the change in the magnetic part of the entropy ΔS_M in a magnetic field 1.8 T (*b*).

($\Delta S^* = R \ln 4 = 11.52$ J/K) [10]. Such discrepancies between experimental data and theoretical values of ΔS^* are typical for manganites and have been repeatedly discussed in the literature [7,15–17].

Figure 3, *a* shows the temperature dependence of the MCE for $La_{0.7}Sr_{0.3-x}Ba_xMnO_3$ in a magnetic field 1.8 T. As can be seen from the figure, with increasing Ba concentration, the temperature of the effect maximum shifts towards lower temperatures, which is in good agreement with the heat capacity data (Fig. 1) and calculations of microscopic parameters. The maximum MCE in the field 1.8 T is $\Delta T_{ad} = 0.86$ K and is observed for the $La_{0.7}Sr_{0.28}Ba_{0.02}MnO_3$ sample at $T = 343$ K. It should be noted that for samples with $x = 0$, 0.02, and 0.05, the MCE varies slightly with doping and varies within $\Delta T_{ad} \sim 0.8$ K. In this case, T_C is shifted by more than 40 K. This means that by adjusting the substitution level, it is possible to obtain the desired T_C in a wide temperature range, while slightly changing the MCE value, which is an important advantage for magnetocaloric materials.

Figure 3, *b* shows the results of studying the temperature dependence of the change in the magnetic part of the entropy, which were obtained from the data on the heat capacity in the field and direct measurements of the MCE using the formula $\Delta S_M = \Delta T_{ad} C_P(T, H)/T$, where ΔT_{ad} — experimental data of direct measurements, $C_P(T, H)$ — temperature dependence of the heat capacity in a magnetic field 1.8 T [18]. The obtained values of ΔT_{ad} and ΔS_m are within the limits given in the literature for other manganites [3,5].

Let us review the mechanisms of heat transfer in more detail. Numerous experimental works have shown that the phononic heat transfer mechanism is dominant in manganites [19–21]. In this case, to analyze the mechanisms of phonon scattering, data on thermal diffusivity can be used. Thermal diffusivity characterizes the rate of temperature

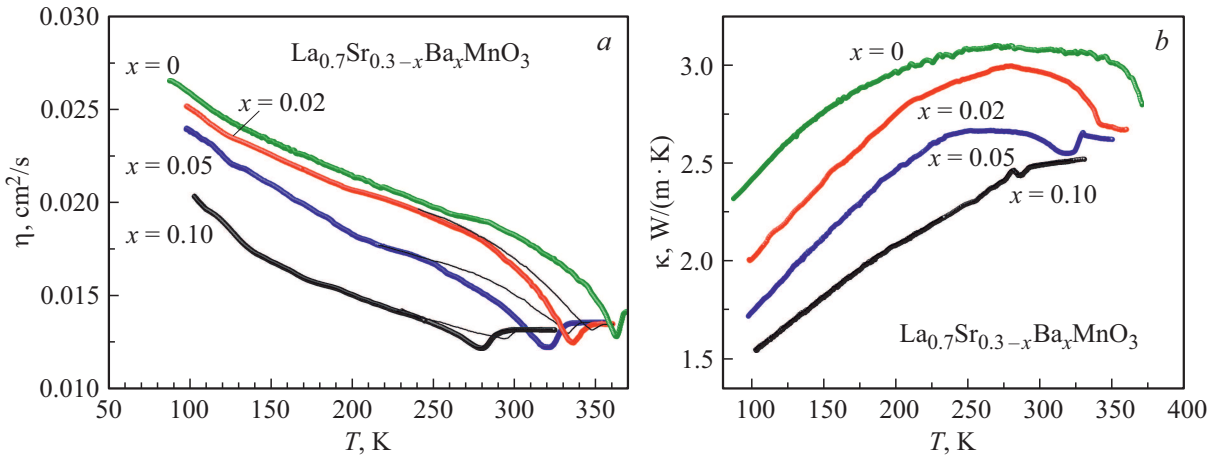

Figure 4. Temperature dependences of thermal diffusivity for $H = 0$ and $H = 1.8$ T (a) and thermal conductivity (b) for $La_{0.7}Sr_{0.3-x}Ba_xMnO_3$ for $H = 0$.

change in non-stationary thermal processes and is related to the phonon mean free path l_{ph} by the relation $\eta = \frac{1}{3} l_{ph} v_s$, where v_s is a sound velocity. Assuming that v_s depends weakly on temperature, using $\eta(T)$ measurements, it is possible to follow the course of $l_{ph}(T)$ and draw appropriate conclusions about the phonon scattering mechanism. The dependence $\eta(T)$ (Fig. 4, a) for all samples near T_C has minima, which are smoothed out in a magnetic field. Such anomalies have already been observed for a number of manganites and were associated with phonon scattering by local distortions of the crystal lattice caused by the Jahn–Teller effect [19,21]. The shape of the minima and their depth, depending on the concentration of Ba and the magnetic field, indicate that, when interpreting the results on heat transfer, it is required to consider several mechanisms that lead to a change in the heat carriers scattering rate.

In the case of phonon scattering only on Jahn–Teller distortions, only a kink without a minimum would be observed on the dependence $\eta(T)$. The shape of the anomalies in the $\eta(T)$ dependences near T_C suggests that, in addition to Jahn–Teller distortions, other mechanisms of phonon scattering should also be reviewed. It can be seen from the figure that the depth of the minimum increases as the distortions of the crystal structure (σ^2) decrease and magnetic fluctuations increase, on the basis of which it can be assumed that phonon scattering by spin fluctuations also takes place. The suitability of such a model for explaining the behavior of $\kappa(T)$ near T_C was demonstrated experimentally in the study of the thermal conductivity of manganite $(La_{1-x}N_{dx})_{0.7}Pb_{0.3}Ca_xMnO_3$ [22], and was theoretically substantiated in the work [23].

The dependence $\kappa(T)$ is shown in Fig. 4 (b). It can be seen that the absolute value of the thermal conductivity increases as the disorder parameter decreases (σ^2) and has a temperature behavior characteristic of manganites [19,21]. The transition to the ferromagnetic phase is accompanied by an increase in κ. A decrease of κ with an increase of σ^2 indicates a significant role of local distortions in limiting the phonon heat flux.

4. Conclusion

The influence of the substitution of the Sr^{2+} ion for the Ba^{3+} ion on the magnetic, thermal, and magnetocaloric properties of $La_{0.7}Sr_{0.3-x}Ba_xMnO_3$ ($x = 0$; 0.02; 0.05; 0.10) manganite has been studied. It is shown that such a substitution leads to an increase in both the disorder parameter σ^2 and the average ionic radius of A-cations $\langle r_A \rangle$, and weakens the intensity of exchange interactions. The abnormal part of the heat capacity and the change in the entropy of the phase transition decreases with increasing concentration of Ba. The thermal conductivity is predominantly phonon in nature and decreases in absolute value as the disorder parameter σ^2 increases.

To explain the observed anomalies in the behavior of thermal diffusivity and thermal conductivity at T_C, it is necessary to involve both the scattering of phonons by local distortions of the crystal lattice, caused by the Jahn–Teller effect, and the interaction of phonons with spin fluctuations. The magnetic field modulation method was used to study the MCE. The data obtained indicate a weak dependence of the effect on the level of substitution, which is of particular practical interest.

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Conflict of interest

The authors have no conflict of interests.

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