
**THERMAL
PROPERTIES**

Effect of Isovalent Cation Substitution on the Thermal, Caloric, and Magnetocaloric Properties of the $(\text{La}_{1-y}\text{Eu}_y)_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ Manganites

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Abstract—Crystalline samples of the $(\text{La}_{1-y}\text{Eu}_y)_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ ($y = 0, 0.2, 0.4, 0.5, 0.6,$ and 0.8) manganite solid solutions have been grown. Temperature dependences of the specific heat, thermal expansion, and high-intensity magnetocaloric effect have been investigated. A comparative analysis of the effect of isovalent cationic substitution on the thermal and caloric parameters of the ferromagnetic phase transition has been made. It has been shown that the growth of the Eu atom concentration leads to a decrease in the phase transition entropy and an increase in the baric coefficient dT/dp . Field and temperature dependences of the magnetocaloric effect have been established. It is demonstrated that, varying the ratio of cations, one can obtain the solid solutions with the maximum magnetocaloric effect value in fields of up to 6 kOe in a temperature range of 90–340 K. Owing to the similar reduced relative cooling powers, the investigated solid solutions can be used as reference solid-state cooling media in designing the cascade cooling systems.

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1. INTRODUCTION

Recently, there has been an increasing need for new high-efficiency cooling devices that would be competitive with gas compressor cooling systems widely used for a long time. This is caused, in particular, by the environmental problems related to the use of freons and requirements for miniaturization of refrigerators and high specific energy efficiency and cooling capacity. One of the most promising directions is the development of refrigerators based on the caloric (electro-, baro-, and magnetocaloric) effects in solids, which consist in the temperature or entropy variation in a material in a switched-on/off external field (electric, magnetic, or stress) [1–8]. The extensive (ΔS_{CE}) and intensive (ΔT_{AD}) caloric effect values are proportional to the temperature derivatives of the order parameter (polarization, strain, and magnetization) [1] and, in view of this, attain their maximum values in the region of phase transitions occurring in ferroic and multiferroic materials.

Solid-state cooling media have a number of advantages over gaseous ones, including the low specific volume, higher ecological tolerance, and significant energy efficiency [1, 9].

In studying different caloric effects in solids, the greatest attention is paid to the magnetocaloric effect (MCE), which is mainly due to the rich variety of magnetic materials and their relatively simple design [10]. Along with the creation of new high-efficiency MCE-based solid-state cooling media, there still has been a keen interest in the family of LaMnO_3 -based manganites with a perovskite structure. Usually, the solid solutions of manganites with mixed-valence cations are synthesized by heterovalent substitution of Ca^{2+} , Sr^{2+} , Ba^{2+} , and Pb^{2+} [11–15] or Na^+ , Ag^+ , and K^+ cations [16–18] for the La^{3+} cation. Due to the presence of a divalent/monovalent cation in the structure, the trivalent state of a part of Mn^{3+} ions changes for the tetra/pentavalent state, which, in turn, leads to the occurrence of the ferromagnetic state, according to the latest model concepts [19]. The manganites known by now are worse than the Gd-based compounds and $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ and $\text{La}(\text{Fe}_x\text{Si}_{1-x})$ alloys [20] in the maximum caloric effect values ΔS_{MCE} and ΔT_{AD} . However, first, they have a comparable relative cooling power (RCP) due to the wide temperature range of the significant MCE and, second, they are cheaper.

An increase in the substituent cation concentration enhances the stability of a ferromagnetic phase, which is brightly pronounced, in particular, in the system of $\text{La}_{1-x}\text{Pb}_x\text{MnO}_3$ solid solutions ($T_C \approx 170$ and 350 K at $y = 0.1$ and 0.3 , respectively) [21]. Studies of the effect of isovalent substitution of rare-earth cations for La^{3+} on the properties of the $(\text{La}_{1-y}\text{Me}_{3+y})_{0.7}\text{Me}_{0.3}^{2+}\text{MnO}_3$ manganites [22–24] showed that this results in the strong destabilization of the ferromagnetic phase and the degree of lowering of the transition temperature T_C depends on the substituent cation size. For example, in the $(\text{La}_{1-y}\text{Eu}_y)_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ (LEPM) compounds, the T_C value decreases from 340 to 120 K upon variation in the concentration of Eu^{3+} cations from 0 to 60% [22]. Such a wide temperature range of the phase transitions in LEPM solid solutions allows them to be considered as reference solid-state cooling media promising for use in cascade cooling cycles.

It is worth noting that the LEPM compounds undergo second-order phase transitions, in contrast to the related $(\text{La}_{1-y}\text{Me}_y^{3+})_{0.7}\text{Me}_{0.3}^{2+}\text{MnO}_3$ (Me^{3+} is Pr, Nd, Gd, Dy, or Tb and Me^{2+} is Ca^{2+} or Ba^{2+}) manganites [15, 24] and many other magnetic materials [20] and, therefore, satisfy one of the basic requirements for solid-state cooling media, specifically, the absence of the transition temperature hysteresis [25].

In this study, we investigated the effect of the ratio between the Eu^{3+} and La^{3+} cation concentrations on the magnetic and thermal properties of the $(\text{La}_{1-y}\text{Eu}_y)_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ ($y = 0, 0.2, 0.4, 0.5, 0.6,$ and 0.8) solid solution system by direct measurements of the specific heat, thermal expansion, and magnetocaloric effect.

2. EXPERIMENTAL

The $(\text{La}_{1-y}\text{Eu}_y)_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ crystalline samples were grown by spontaneous crystallization [19]. The PbO and PbF_2 mixture was used as a solvent and ensured a desired number of Pb atoms in the crystals. To obtain polycrystalline samples, the initial single crystals were subjected to grinding in an agate mortar and pressed in tablets, which were fired at a temperature of 600°C for 3 h. According to the scanning electron microscopy data, the average crystallite size was about $1\text{--}2$ μm . The crystal composition was confirmed by X-ray fluorescence analysis. Phase identification and determination of the lattice parameters were performed on a Bruker D8 ADVANCE X-ray powder diffractometer. The X-ray diffraction patterns showed that the crystals are single-phase. All the X-ray diffraction patterns of the solid solutions with Eu^{3+} reveal a distorted perovskite structure (sp. gr. $P4/m$), while the initial $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ compound has a rhombohedral structure (sp. gr. $R3c$).

The most convenient tool for studying the specific heat and magnetocaloric effect is an adiabatic calorimeter, which allows one to obtain information on these properties in experiments simultaneously conducted on one sample. In this work, an automated calorimeter was used, the design of which was described in detail in [26].

The specific heat $C_p(T)$ was investigated by a technique of discrete (with a step of $1\text{--}3$ K) and continuous ($dT/dt \approx 0.01\text{--}2.0$ K/min) heating in the temperature range of $90\text{--}370$ K. The specific heat determination error was no larger than $0.5\text{--}1.0\%$. The samples were placed in a measuring cell and fixed with ApiezonN and ApiezonH greases, which ensured a reliable heat contact. At temperatures below 90 K, the specific heat of several samples was measured using a universal Quantum Design Physical Property Measurement (PPMS).

The magnetocaloric effect was examined using a previously developed technique in the switched-on and off magnetic field modes at temperatures above and below the phase transition temperature [26]. At a certain temperature, the adiabatic calorimeter was tuned such as to the sample temperature drift was within $dT/dt \leq |10^{-3}|$ K/min for, at least, an hour and similar to linear. This temperature behavior showed that the cryostat conditions were maximally similar to adiabatic: the system was stabilized in the dynamic equilibrium. In this case, the maximum sensitivity to the sample temperature variations was no worse than 10^{-4} K, while an absolute temperature measurement error of $\pm 10^{-2}$ K was limited by the parameters of platinum thermometers used in the cryostat.

At switching-on/off the magnetic field, a magnetic material releases (absorbs) heat spent on changing the temperature of the entire measured system sample + cells + grease. Thus, in the experiments with varying magnetic field, we measure the ΔT_{exp} value that is lower than the real ΔT_{AD} value corresponding to the intensive MCE in the LEPM sample. These temperature effects are related as

$$\Delta T_{\text{AD}} = \Delta T_{\text{exp}} \left(1 + \frac{C_{\text{cell}} + C_{\text{Ap}}}{C_{\text{sample}}} \right), \quad (1)$$

where C_{cell} , C_{Ap} , and C_{sample} are the cell, grease, and sample specific heats, respectively.

The dilatometric investigations were carried out on the polycrystalline samples with sizes of $L = 1.5\text{--}3.0$ mm on an NETZSCH DIL-402C induction dilatometer in the dry helium gas flow. The sample heating rates in the temperature range of $100\text{--}500$ K were from 2 to 4 K/min. A fused quartz reference was used for calibrating and taking into account the expansion of the measuring system. The data obtained in several measurement series were consistent with each other within $2\text{--}5\%$.

3. RESULTS AND DISCUSSION

Figure 1a presents the results of calorimetric study in a wide temperature range in the form of the LEPM solid solution specific heats, which almost coincide beyond the anomalous temperature regions.

Due to the small difference between the lanthanum and europium atomic masses, the difference between molar masses of the solid solutions with the y value from 0 to 0.8 and, correspondingly, molar specific heats, was found to be very small ($\sim 3\%$). In the scale chosen in Fig. 1a, the most clear are the $C_p(T)$ anomalies related to the transition between the paramagnetic and ferromagnetic phases in the $(\text{La}_{1-y}\text{Eu}_y)_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ ($y = 0, 0.2, \text{ and } 0.5$) compounds. In this case, the most informative are the anomalous contributions $\Delta C_p(T)$ to the specific heat, which are extracted by considering the specific heat of the solid solutions far from T_C to be a regular/lattice contribution C_{LAT} to the total specific heat $C_p(T)$. The lattice component of each solid solution was determined by interpolating the data in individual temperature ranges using a combination of the Debye and Einstein functions. For all the compositions, the $C_{\text{LAT}}(T)$ dependences were identical with the similar Debye and Einstein temperatures: $\Theta_D \sim 213$ K and $\theta_E \sim 525$ K. The extraction of the anomalous specific heat $\Delta C_p(T) = C_p(T) - C_{\text{LAT}}(T)$ (Fig. 1b) made it possible to determine the $\Delta C_p(T)$ maxima, which were assumed to be the phase transition temperatures, for each the LEPM component (Table 1).

It can be seen in Fig. 1b that the Eu^{3+} concentration growth leads to spreading of the specific heat peak and a significant decrease in its maximum value: ΔC_p from 90 mJ/g K at $y = 0$ to 7 mJ/g K— $y = 0.8$. Accordingly, the phase transition enthalpies ΔH determined by integrating the area under the $\Delta C_p(T)$ peak are also significantly reduced (Table 1). However, the anomalous entropies related to the phase transition and determined by the combination of the ratios between the specific heat, enthalpy, and transition temperature $\Delta S = \int (\Delta C_p/T) dT \approx \Delta H/T_C$ appeared to be less sensitive to the isovalent cation substitution. Moreover, the ΔS value decreases by a factor of ~ 3.5 only when y increases from 0 to 0.5 and remains almost invariable with a further increase in the Eu^{3+} concentration within the determination error. This is caused by a sharp decrease in the transition temperature (Fig. 2a).

The decrease in the phase transition entropy can be explained in the thermodynamic theory approximation [27], according to which this value is proportional to the squared order parameter (magnetization in the case of LEPM) $\Delta S(T) = A_T M^2(T)$. Here, A_T is one of the coefficients of the thermodynamic potential $\Delta\Phi = A_T M^2 + BM^2 + CM^2 + \dots + HM$ determined by the derivative of the inverse magnetic susceptibility $d\chi^{-1}/dT$. According to [19], for a solid solution with $y = 0.6$, the

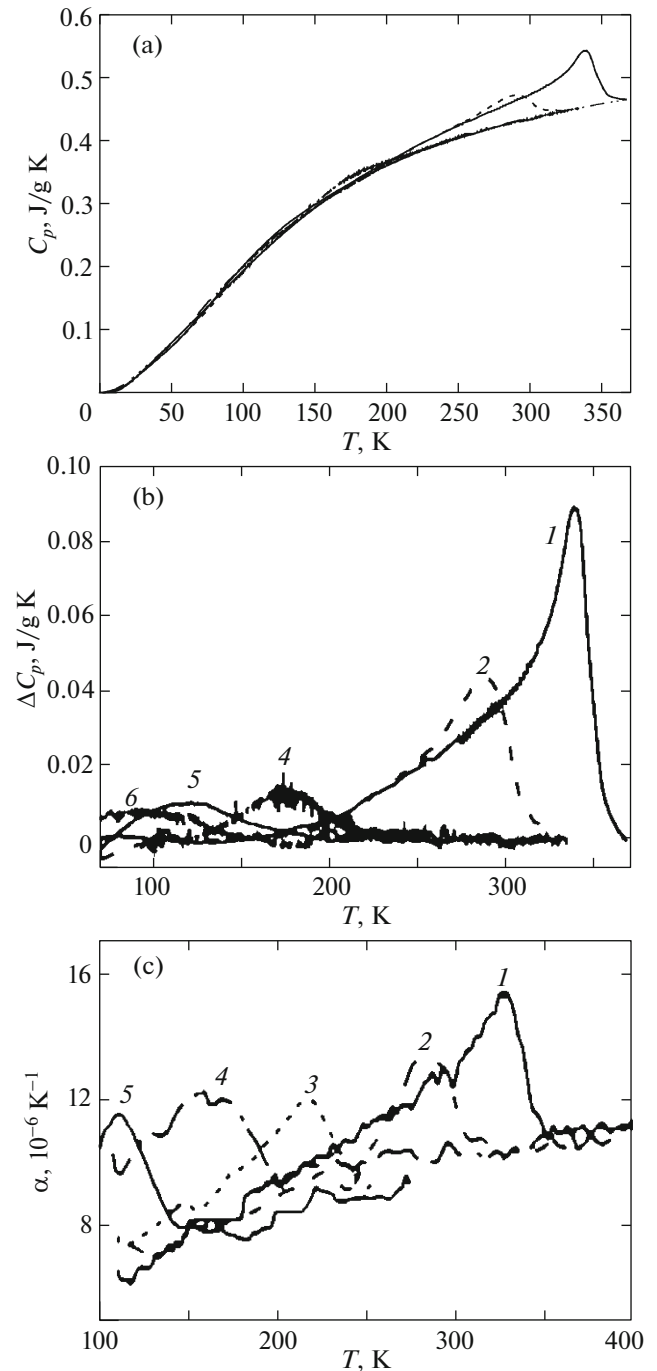


Fig. 1. Temperature dependences of (a) specific and (b) anomalous heat and (c) thermal expansion coefficient of the $(\text{La}_{1-y}\text{Eu}_y)_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ solid solutions with $y = (1) 0, (2) 0.2, (3) 0.4, (4) 0.5, (5) 0.6, \text{ and } (6) 0.8$.

M value is approximately twice as low as in $\text{La}_{0.7}\text{Pb}_{0.3}\text{ZMnO}_3$, which should lead to a fourfold entropy drop similar to the ΔS variation observed by us (Fig. 2b).

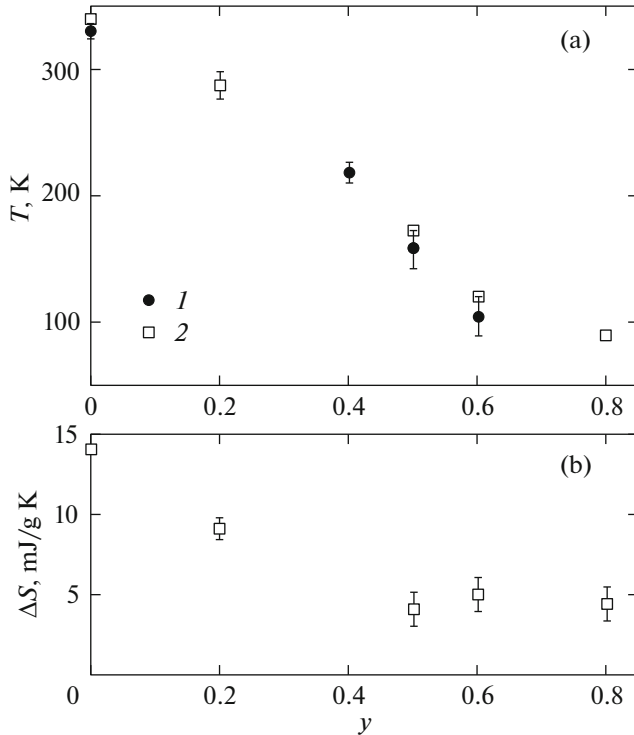
The temperature dependences of the linear thermal expansion coefficient $\alpha(T)$ of the solid solutions are

Table 1. Some thermodynamic parameters of the phase transition in the $(\text{La}_{1-y}\text{Eu}_y)_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ solid solutions

y	T_C , K	ΔH , J/g	dT/dp , K/kbar
0	339	4.70	0.8
0.2	287	2.60	1.0
0.5	172	0.70	1.6
0.6	120	0.63	2.3
0.8	90	0.44	—

shown in Fig. 1c. Due to the small linear sizes of the samples, the measurement error appeared to be fairly large (5–10%). For each LEPM composition, one small $\alpha(T)$ anomaly was detected, the maximum temperature of which taken as a phase transition temperature decreases with increasing y . In accordance with the concentration phase diagram, the $T_C(y)$ dependences determined in the calorimetric and dilatometric experiments are fully identical (Fig. 1c), which shows the high reliability of the data obtained using different methods.

It follows from the $\alpha(T)$ dependences (Fig. 1c) that, in contrast to the specific heat ΔC_p , the values of thermal expansion coefficient anomalies change slightly upon variation in the ratio between lanthanum

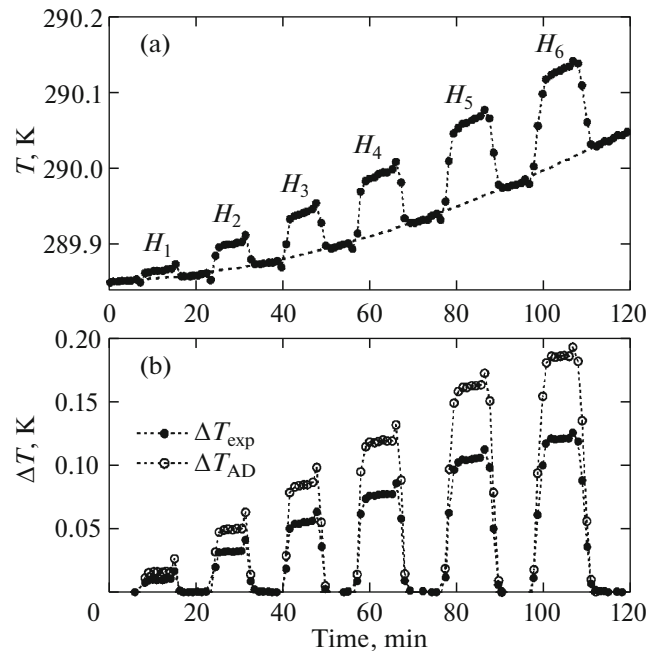
**Fig. 2.** Dependences of (a) the temperature and (b) enthalpy of the phase transition on the Eu^{3+} cation concentration.

and europium concentrations. The positive sign of α anomalies is indicative of an increase in the volume during the transition to the paramagnetic phase.

The phase transition in the LEPM solid solutions is a typical second-order transformation. Therefore, using the Ehrenfest equation $dT_C/dp = T_C(\Delta\beta/\Delta C_p)$ and detailed calorimetric and dilatometric data and making the assumption $\Delta\beta = 3\Delta\alpha$, one can obtain information on the susceptibility of the compounds to the external hydrostatic pressure. The calculated initial phase transition temperature shifts under hydrostatic pressure (Table 1) are indicative of an increase in the baric coefficient with increasing Eu^{3+} concentration.

Figure 3a presents the results of one of the intensive MCE measurement series performed in the paramagnetic phase in the vicinity of 290 K on the sample with $y = 0.2$ in magnetic fields from 1 to 6 kOe. The average rate of the temperature variation related to the intrinsic temperature course of the calorimeter was $dT/dt \approx 7 \times 10^{-4}$ K/min during the experiment (120 min).

Obviously, the investigated solid solution exhibits a noticeable intensive magnetocaloric effect: switching on (off) the magnetic field is accompanied by a reliably detectable increase (decrease) in the temperature of the system sample + cell + grease. The degree of MCE reversibility was found to be quite high: after

**Fig. 3.** Time dependences of (a) the $(\text{La}_{0.8}\text{Eu}_{0.2})_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ sample temperature and (b) high-intensity magnetocaloric effect ΔT_{AD} upon switching on and off the magnetic field: $H_1 = 1.2$ kOe, $H_2 = 2.2$ kOe, $H_3 = 3.3$ kOe, $H_4 = 4.1$ kOe, $H_5 = 5.4$ kOe, and $H_6 = 6.0$ kOe.

switching off the magnetic field, the system temperature returns to the expected level obtained by the extrapolation of the temperature course dT/dt from the temperature region preceding the field switching-on.

At the instants of switching on and off the magnetic field, the abrupt stepwise temperature changes (splashes) were observed, which have signs opposite to the MCE sign and related to the voltage induced on a high-sensitivity amplifier of a thermocouple signal in the temperature control circuit. The constant temperature course dT/dt under the conditions $H = 0$ and $H \neq 0$ shows that this effect in no way affects the reliability of regulation of the adiabatic conditions. The experiments conducted at the same temperatures in the oppositely directed magnetic fields showed the invariability of the sign and value of both the intensive MCE and temperature splashes, which confirms their nonphysical nature.

Figure 3b illustrates the correlation between the experimental temperature changes ΔT_{exp} and ΔT_{AD} corrected with regard to Eq. (1).

Similarly, we measured the intensive MCE for the other LEPM compositions in the vicinity of individual phase transitions. The temperature dependences of ΔT_{AD} in magnetic fields of 3.2, 4.1, and 4.8 kOe for the investigated solid solutions are shown in Fig. 4.

Note a peculiar character of the ΔT_{AD} changes with increasing Eu^{3+} concentration. A sharp decrease in the maximum intensive MCE in the compound with $y = 0.2$ as compared with $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ is followed by a slight change in its value in the other solid solutions.

However, in the solid solution with $y = 0.8$, the $\Delta T_{\text{AD}}^{\text{MAX}}$ value was found to be larger by $\sim 20\%$ than in the composition with $y = 0.6$ and was observed in a narrower temperature range (Fig. 4). The established features can be attributed to the fact that the MCE intensity is determined by the relation between the temperature, specific heat, and temperature derivative of magnetization [1]

$$\Delta T_{\text{AD}} = -\frac{T}{C_p} \left(\frac{\partial M}{\partial T} \right)_H dH. \quad (2)$$

Obviously, the combination of these values can be significantly affected by the sample quality, which, in the case of solid solutions, is determined, to a great extent, by the homogeneity of the ordering of the substituent Eu^{3+} cation in the manganite crystal lattice. In addition, it follows from Eq. (2) that, under certain conditions, the $\Delta T_{\text{AD}}(H)$ dependence can be almost linear (Fig. 5a).

More informative, however, is the field dependence of the reduced $(\Delta T_{\text{AD}}/H)(H)$ value (Fig. 5b). It can be seen that the effect of the coercive field in the solid solutions is significantly weaker (~ 1 kOe) than in $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ (3 kOe).

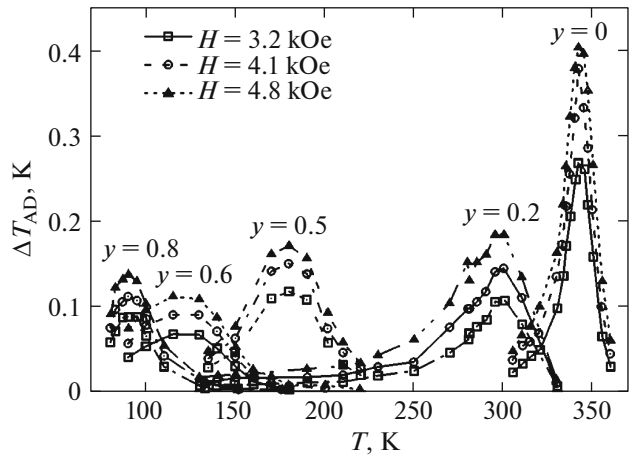


Fig. 4. Temperature dependences of the high-intensity magnetocaloric effect ΔT_{AD} in the $(\text{La}_{1-y}\text{Eu}_y)_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ manganites at different magnetic-field strengths.

The efficiency of a magnetic cooling medium is determined not only by the absolute MCE value, but also by the temperature ranges in which the ΔT_{AD} and ΔS_{MCE} values are relatively large. Therefore, the most objective parameters for comparing the efficiencies of different magnetocaloric materials are the integral characteristics, i.e., the relative cooling powers (RCPs) [1]

$$\text{RCP}(T) = \Delta T_{\text{AD}}^{\text{max}} \delta T_{\text{FWHM}}, \quad (3)$$

$$\text{RCP}(S) = \Delta S_{\text{MCE}}^{\text{max}} \delta T_{\text{FWHM}}, \quad (4)$$

where $\Delta T_{\text{AD}}^{\text{max}}$ and $\Delta S_{\text{MCE}}^{\text{max}}$ are the maximum intensive and extensive MCE values and δT_{FWHM} is the full width at half maximum of $\Delta T_{\text{AD}}^{\text{max}}(T)$ and $\Delta S_{\text{MCE}}^{\text{max}}(T)$.

The field dependences of the relative cooling powers reduced to the field values $\text{RCP}(T)/H$ and $\text{RCP}(S)/H$ are shown in Figs. 5c and 5d. The most effective cooling medium was found to be the solid solution with $y = 0.5$ with the parameters RCP/H higher by 30% than in $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ and the solid solutions with $y = 0.2$ and 0.6. Due to the wide temperature range of the similar $\Delta T_{\text{AD}}^{\text{max}}$ values and small magnetic field strengths leading to the almost constant $\text{RCP}(T)/H$ and $\text{RCP}(S)/H$ values, the system of the $(\text{La}_{1-y}\text{Eu}_y)_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ solid solutions can be considered as a reference in designing the cascade cooling cycles based on solid-state cooling media.

4. CONCLUSIONS

Thus, the effect of isovalent cationic substitution on the specific heat, thermal expansion, MCE, and RCP of the $(\text{La}_{1-y}\text{Eu}_y)_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ (in: 0, 0.2, 0.4, 0.5, 0.6, 0.8) manganite solid solutions was investigated.

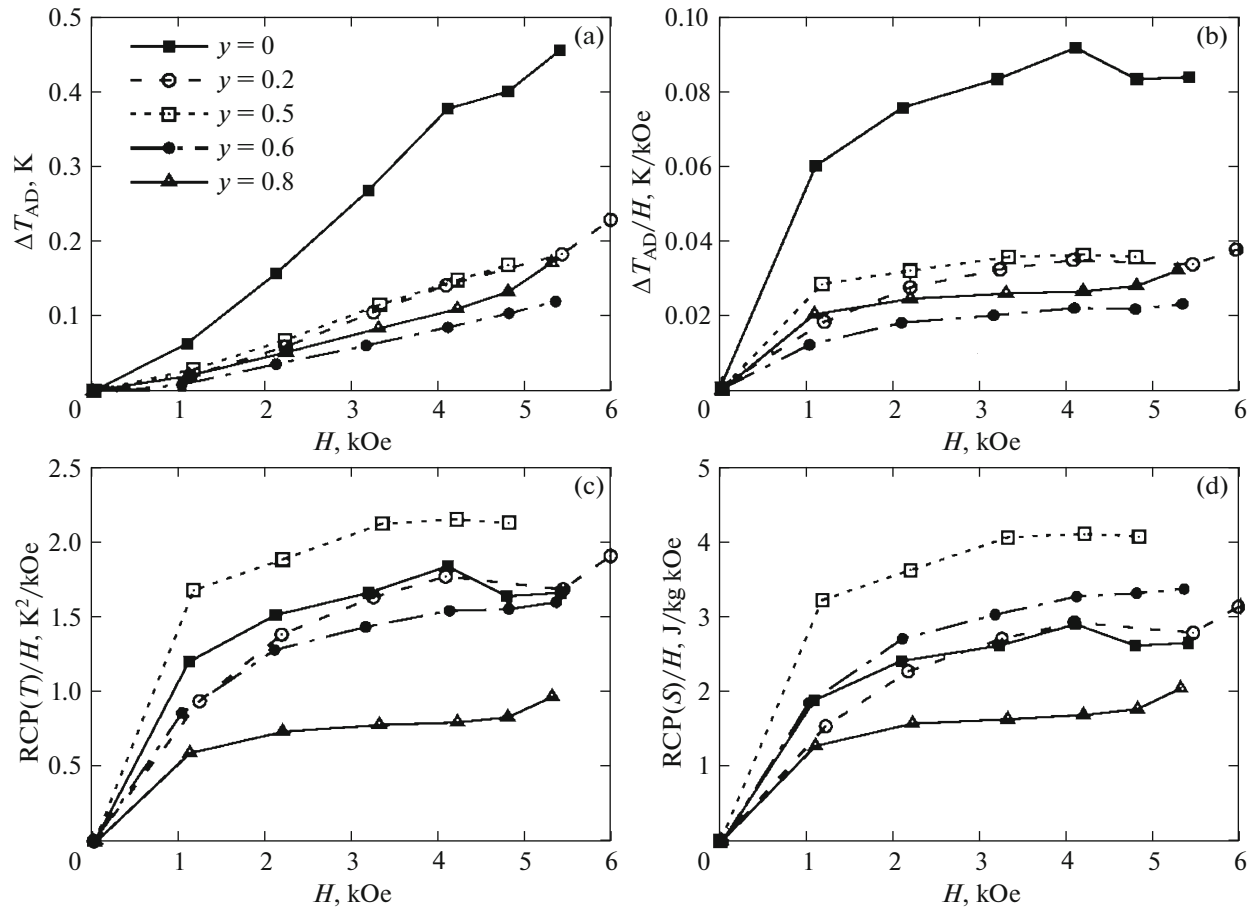


Fig. 5. Magnetic field dependences of the absolute and reduced (a) high-intensity ΔT_{AD} and (b) $\Delta T_{AD}/H$ magnetocaloric effects and reduced relative cooling power (c) $RCP(T)/H$ and (d) $RCP(S)/H$.

A significant decrease in the ferromagnetic phase transition temperature and in the maxima of the specific heat anomalies with increasing Eu^{3+} cation concentration was found. The thermal expansion coefficient anomalies change much weaker. According to the Ehrenfest equation, this leads to an increase in the susceptibility of the solid solutions to the hydrostatic pressure.

Despite a significant decrease in the phase transition enthalpy with the change in y from 0 to 0.8, the entropy of the solid solutions was found to be less sensitive to the cationic substitution and, at $y \geq 0.5$, remains almost invariable due to a sharp decrease in the transition temperature.

Varying the $\text{Eu}^{3+}/\text{La}^{3+}$ cation ratio from 0 to 0.8, one can obtain solid solutions with the maximum MCE in a very wide temperature range, from 340 K to 90 K.

According to the similar absolute values of ΔT_{AD}^{\max} in the same field for the solid solutions with $y = 0.2$ –0.8 and constant $RCP(T)/H$ and $RCP(S)/H$ values implemented in weak fields, the system of solid-state

$(\text{La}_{1-y}\text{Eu}_y)_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ cooling media can be recommended as the initial one in modeling cascade cooling cycles.

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