

Magnetization and magnetocaloric effect in $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ ceramics and $0.85(\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3)-0.15(\text{PbTiO}_3)$ composite

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The magnetization behavior under temperature and magnetic field variation was investigated for $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ ceramics and ferromagnetic–ferroelectric $0.85(\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3)-0.15(\text{PbTiO}_3)$ composite. The second-order ferromagnetic phase transition in manganite is shifted to the tricritical point in composite material. Comparison of the intensive caloric effect and the difference between relative cooling powers (RCP) in both materials proves a significant role of intrinsic pressure in elevating caloric efficiency in composite induced by elastic coupling between the grains of LPM and PT components. No temperature change in composite under an electric field of 2 kV/cm associated with electrocaloric effect or indirect magnetoelectric coupling was observed. The effect of magnetic field on some peculiar temperatures is considered. A contribution from pressure generated by magnetic field to baric coefficient dT/dp of ferromagnetic transformation temperature in composite was suggested. The results obtained were analyzed in the framework of the magnetic equation of state and compared with the experimentally measured heat capacity.

I. INTRODUCTION

Solids exhibiting caloric effects (CE) associated with the reversible change of temperature ΔT_{AD} or entropy ΔS_{CE} under external field (magnetic H , electric E , mechanical stress σ , or hydrostatic pressure p) at constant entropy and temperature, respectively, attract considerable attention because of their potential possibilities for use as working bodies in thermodynamic cycles of modern and effective alternative solid-state refrigeration technologies. Over a long period of time, the main purpose of investigations was to reveal the materials-refrigerants with a giant magneto-CE (MCE)^{1–3} and electro-CE (ECE).^{4–6} Currently, investigators were also interested in the barocaloric effect (BCE), partially because of its versatility.^{7–10} Indeed, such an effect can be realized in materials of distinct physical nature.

The dependences of both extensive ΔS_{CE} and intensive ΔT_{AD} CE on the generalized ferroic order parameter Y (magnetization, polarization, and elastic deformation) and conjugated external field X are described by the following equations:¹

$$\Delta S = \int \left(\frac{\partial Y}{\partial T} \right)_X dX, \quad (1)$$

$$\Delta T = - \int \frac{T}{C_X} \left(\frac{\partial Y}{\partial T} \right)_X dX. \quad (2)$$

The largest value of $(\partial Y/\partial T)_X$ derivative is in ferroic materials (ferromagnets, ferroelectrics, and ferroelastics) in the temperature region near phase transitions close to the tricritical point.¹

Because very often ferromagnetic and ferroelectric phase transitions in monoferroic materials are followed by anomalous behavior of thermal expansion, one can elevate the ΔT_{AD} and ΔS_{CE} values using the external hydrostatic or uniaxial pressure in addition to magnetic or electric field. To our knowledge, in spite of such an evident fact, there are rather few attempts to study the CE of the different nature in the same material. For example, investigations of MCE and BCE were performed in $\text{Fe}_{49}\text{Rh}_{51}$ and Heusler shape memory alloys^{11–13} as well as in compounds $\text{R}_5\text{Si}_2\text{Ge}_2$ ($\text{R} = \text{Tb}, \text{Gd}$).^{14,15}

Single-phase multiferroic compounds consisting of two or three different ferroic subsystems are suggested now to be considered as multicaloric materials which are the most promising ones to be used as solid-state refrigerants.^{16–19} First, the caloric properties of such materials can be

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improved using simultaneously several external fields. Second, thanks to magnetoelectric, magnetoelastic, or electroelastic coupling, the lifting of distinct or integrated intensive and extensive CE can be controlled by one of three external fields.

Composites involving ferromagnetic and ferroelectric components are also interesting and useful materials to obtain integrated CE. In that case, the interaction between two phases is indirectly generated by mechanical stress appearing under external fields on the boundaries of intimately connected grains or layers.

Recently, we have studied two CE in ferroelectric $\text{PbTiO}_3 - \text{PT}$ (ECE and BCE)¹⁶ and ferromagnetic $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3 - \text{LPM}$ (MCE and BCE)²⁰ as well as three CE in volumetric multiferroic composites $x\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3-(1-x)\text{PbTiO}_3$ ($x = 0.85; 0.18$) (LPM-PT).²¹ It was found that ECE at ferroelectric phase transition in LPM-PT at least at low electric fields (<3 kV/cm) increases compared to this effect in pure PT. One more interesting peculiarity was connected with the increase of intensive MCE in composites at phase transition between para- and ferromagnetic phases near 340 K. The difference between ΔT_{AD} values for LPM-PT and LPM was increased in the range of magnetic fields studied. The electric polarization in PT component changes near temperature of ferromagnetic phase transition very slowly with variation in the temperature.²² In such a case, in accordance with the equation¹⁷

$$dT = -\frac{T}{C_{p,E,H}} \left[\left(\frac{\partial M}{\partial T} \right)_{p,E,H} + \text{IMEC} \left(\frac{\partial P}{\partial T} \right)_{p,E,H} \right] dH \quad , \quad (3)$$

the contribution from indirect magnetoelectric coupling (IMEC) associated with the $(\partial P/\partial T)_{E,H}$ polarization derivative to the total ΔT_{AD} value generated by magnetic field is negligible. Taking into account this fact, it was possible to suppose that the additional contribution to the intensive CE ΔT_{AD} in LPM-PT results from BCE under pressure generated by the elastic mechanical interaction between magnetostrictive and piezoelectric phases.²¹

In the present work, we prolonged the investigation of the nature of the magnetocaloric efficiency increase in ferromagnetic-ferroelectric material. The study of the temperature and magnetic field dependencies of magnetization was carried out on LPM ceramics and multiferroic $0.85\text{LPM}-0.15\text{PT}$ composite. The results were analyzed using Eq. (2) and the magnetic equation of state to compare them with experimental data on intensive MCE and heat capacity obtained by us earlier in direct measurements.²¹

II. EXPERIMENTAL

Magnetic measurements under temperature and magnetic field variation were performed on the LPM and LPM-PT samples fabricated by the standard ceramic technology and used in our previous direct studies on the intensive MCE in an adiabatic calorimeter.²¹ The LPM component was prepared by grinding of single crystals studied earlier by us.²⁰ It was very important because we were able to see the effect of the sample state on the physical properties. The sintering of the samples under study at rather low temperature (800 °C) allowed us to avoid the formation of solid solutions and the interdiffusion processes in composite. The x-ray characterization proved that diffraction peaks observed in composite material correspond to the sum of rhombohedral LPM and tetragonal perovskite PT phases. No foreign phases were found.

Examination of the samples using a scanning electron microscope showed that the largest amount of grains in LPM and LPM-PT ceramics has size below 10 μm .²¹ The relative density of both ceramic samples was about 90%.

The magnetization measurements were carried out from 3 to 370 K under fields in the range of 1–15 kOe using a commercial quantum design physical properties measurement system (PPMS).

III. RESULTS AND DISCUSSION

The $M(T)$ data for both samples were collected on cooling ($H = 1, 5, 15$ kOe) [Figs. 1(a) and 1(b)] and heating ($H = 3, 10$ kOe) [Figs. 1(c) and 1(d)]. The magnetization of the LPM-PT composite is presented as converted for the pure LPM component. Figure 1 shows that apart from strong increase of magnetization in the region of phase transition, a small step-wise anomaly was detected from the $M(T)$ curves at all fields in the range of 40–70 K. The same low temperature peculiarity of magnetization behavior was also observed in the LPM single crystal as well as in the $(\text{La}_{1-y}\text{Eu}_y)_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ and $\text{La}_{0.55}\text{Bi}_{0.15}\text{Ca}_{0.3}\text{MnO}_3$ solid solutions.^{23,24} However, no anomalous heat capacity behavior was found in a corresponding temperature range.^{20,24}

The saturated M value of the LPM-PT composite at $H = 1$ kOe is slightly less than that of LPM ceramics. This difference decreases with increase in the magnetic field and almost disappears at 5 kOe (Fig. 1). On the other hand, the minimum value of the $(\partial M/\partial T)_H$ derivative for LPM-PT is less than the same parameter for LPM, for instance for $H = 1, 5,$ and 15 kOe, as can be seen in Fig. 2. The faster change in magnetization with temperature in LPM-PT means that the second-order phase transition observed in LPM ceramics²¹ is shifted to the

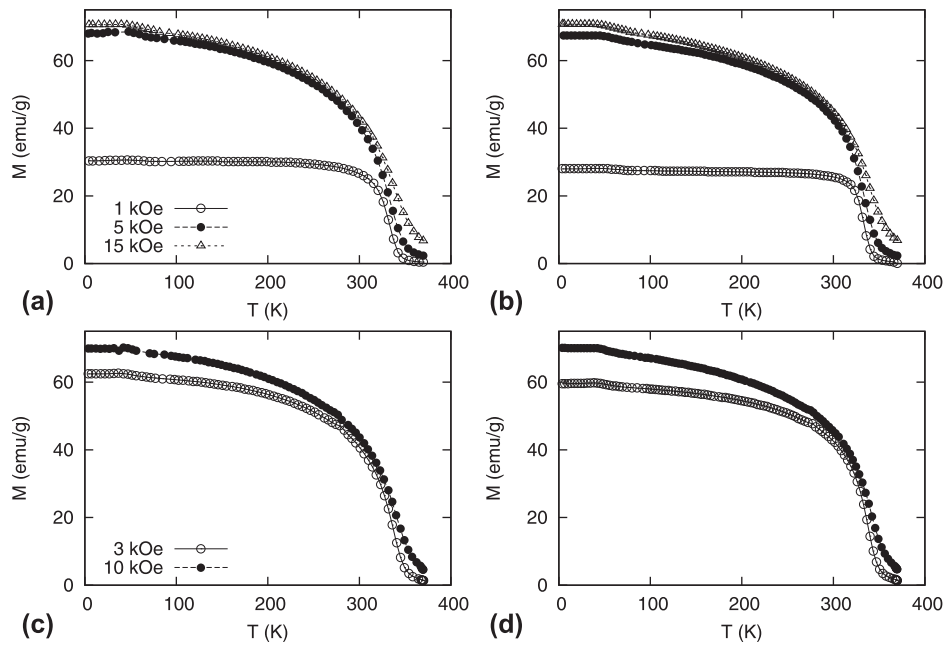


FIG. 1. Temperature dependences of magnetization measured on cooling (a, b) and on heating (c, d) of LPM (a, c) and LPM-PT (b, d).

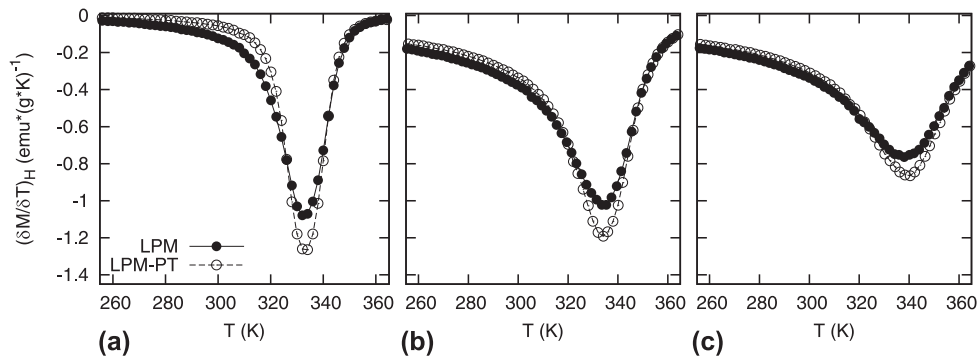


FIG. 2. Temperature dependences of $(\partial M / \partial T)_H$ for LPM and LPM-PT at different magnetic fields: 1 kOe (a), 5 kOe (b), and 15 kOe (c).

tricritical point in composite. It is necessary to point out that the elevating field strength from 1 to 15 kOe, on the one hand, decreases the modulus $(\partial M / \partial T)_H$ values and, on the other, does not change significantly the relationship between these derivatives at the minimum point for LPM-PT and LPM, namely, from 1.18 to 1.13. Hence, the magnetic field does not affect strongly on the closeness of phase transitions to the tricritical point in these materials.

From our point of view, the reason for the large modulus value of $(\partial M / \partial T)_H$ in LPM-PT compared to LPM is most likely associated with the mechanical stress appearing on the boundary between ferroelectric and magnetic grains in the composite. There are at least two possible sources of pressure generation. They are connected with a magnetostrictive effect in LPM phase and/or with large difference in thermal expansion $\Delta V / V$ of LPM and PT components in composite in the phase transition region in LPM.^{16,20}

Argument in support of the latter hypothesis can be obtained from the comparison of the unit cell volumes of manganites $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ (59.4 \AA^3) and $\text{La}_{0.69}\text{Ca}_{0.31}\text{MnO}_3$ (54.7 \AA^3).^{23,25} The homovalent $\text{Ca}^{2+} \rightarrow \text{Pb}^{2+}$ substitution is followed by both the chemical pressure increase and the change of the phase transition from the second-order to the first one. One more interesting example of phase transition order change one can see analyzing the results of magnetization measurements in the series of solid solutions $\text{La}_{1-x}\text{Pb}_x\text{MnO}_3$ ($x = 0.1; 0.2; 0.3$).²⁶ The heterovalent $\text{Pb}^{2+} \rightarrow \text{La}^{3+}$ substitution is accompanied by the unit cell volume increase ($58.1 \text{ \AA} \rightarrow 59.4 \text{ \AA}$) with an increase in the Pb concentration as well as by the shift of the second-order phase transition to the tricritical point.

The information about volume magnetostriction in manganites was obtained by analysis of the $M(H)$

dependencies at $p = 0$ and under pressure in related manganites $\text{La}_{0.69}\text{Ca}_{0.31}\text{MnO}_3$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$.^{25,27} From the expression of the Gibbs free energy,

$$d\Phi = -SdT + vdp - MdH \quad (4)$$

one can obtain differential equation for magnetostriction

$$(\partial v/\partial H)_{p,T} = -(\partial M/\partial p)_{H,T} \quad (5)$$

Because the phase transition temperature increases under pressure in $\text{La}_{0.69}\text{Ca}_{0.31}\text{MnO}_3$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$,^{25,27} the $(\partial M/\partial p)_{H,T}$ derivative is positive and, in accordance with (5), the magnetic field increase is accompanied by the volume decrease. We have found that at $\Delta H = 30$ kOe and $\Delta p = 1.1$ GPa, the relative volume change $\Delta V/V$ near phase transition point in $\text{La}_{0.69}\text{Ca}_{0.31}\text{MnO}_3$ is less than 4×10^{-4} .

On the other hand, the positive thermal deformation $\Delta V/V$ in LPM, determined by us,²⁰ is about an order of magnitude higher ($\sim 6 \times 10^{-3}$) in the ferromagnetic phase transition region than in PT component $\Delta V/V \approx 10^{-3}$.¹⁶ Large difference in thermal expansion is the reason for the appearance of elastic mechanical interaction between LPM and PT components at temperature change of composite leading to pressure generation. Because composites are inhomogeneous materials, the pressure appeared is most likely to be not hydrostatic. Such a hypothesis is supported by the experimental studies of single-phase manganites,^{25,27} where no strong effect of hydrostatic pressure on magnetization behavior

in single-phase $\text{La}_{0.69}\text{Ca}_{0.31}\text{MnO}_3$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ compounds was observed.

In accordance with (1) and (2), the difference between the $(\partial M/\partial T)_H$ values close to phase transition point in LPM and LPM-PT leads to different MCE in both materials. The information on intensive MCE ΔT_{AD} was obtained by analysis of the $M(T)_{H=\text{const}}$ dependences using (2) and the heat capacity data studied experimentally by us earlier.^{20,21} Figures 3(a) and 3(b) show that the calculated intensive MCE in both materials exceeds ΔT_{AD} values obtained in direct measurements by an adiabatic calorimeter.²¹ Taking into account that experimental and calculated ΔT_{AD} were determined at a little bit of different fields, the difference between both ΔT_{AD} values may be considered as the modest one. Moreover, the detailed analysis of different methods of the MCE determination²⁸ showed that the combined relative error in the MCE values calculated using the $M(T,H)$ data can reach 10%, as it was observed, for example, for $\text{La}_{0.55}\text{Bi}_{0.15}\text{Ca}_{0.3}\text{MnO}_3$.²⁴

Figure 3(c) shows that calculated intensive MCE in composite exceeds that in pure LPM at all fields studied, as it was found also in direct measurements. With reference to Fig. 3(d), it can be seen that the differences between the maximum values of $\Delta T_{AD}^{\text{max}}$ calculated as well as measured for LPM and LPM-PT are close to each other. In line with these results, one can think that the pressure generated by elastic mechanical interaction between ferromagnetic and ferroelectric components leads only to the shift of phase transition

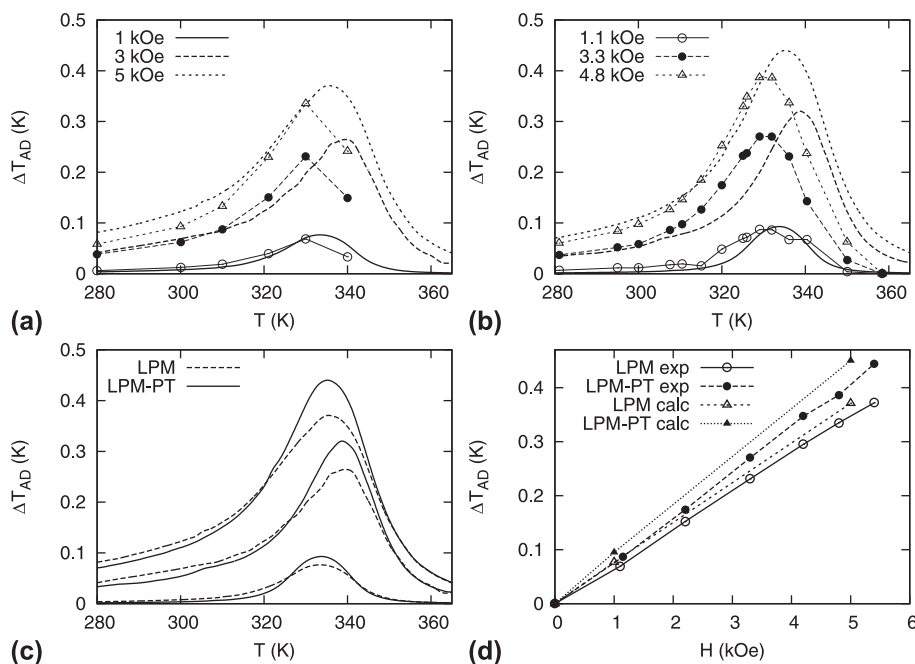


FIG. 3. Temperature dependences of measured (dots) and calculated (lines) ΔT_{AD} for LPM (a) and LPM-PT (b). Comparison of calculated ΔT_{AD} for LPM and LPM-PT (c). Field dependences of calculated (calc) and measured (exp) $\Delta T_{AD}^{\text{max}}$ for LPM and LPM-PT (d).

to the tricritical point. To make sure that this is not the case, we estimated the integrated caloric parameters called as relative cooling power (RCP)¹

$$\text{RCP}(T) = \Delta T_{\text{AD}}^{\text{max}} \times \delta T_{\text{FWHM}} \quad (6)$$

$$\text{RCP}(S) = -\delta S_{\text{CE}}^{\text{max}} \times \delta T_{\text{FWHM}} \quad (7)$$

Here, δT_{FWHM} is the full-width at the half maximum of the $\Delta T_{\text{AD}}(T)$ and $\Delta S_{\text{MCE}}(T)$ curves.

In Table I, the $\text{RCP}(T)$ and $\text{RCP}(S)$ values determined at $H = 5$ kOe using experimental data on $\Delta T_{\text{AD}}^{\text{MCE}}(T, H)$ and $M(T, H)$ are presented for LPM and LPM-PT. One can see that both values evaluated by analysis of magnetization (calc) exceed those obtained from experimental intensive MCE (exp). It was also found that “experimental” values of $\text{RCP}(T)$ and $\text{RCP}(S)$ are higher in composite compared with LPM, whereas for “calculated” values there is opposite situation. Taking into account the discussion on the error of MCE evaluation from magnetization measurements,²⁸ it is better to consider the field dependence of the difference between RCP values for composite and manganite $\Delta \text{RCP} = \text{RCP}^{\text{LPM-PT}} - \text{RCP}^{\text{LPM}}$. As seen from Fig. 4, the field increase is followed by decrease of both $\Delta \text{RCP}_{\text{calc}}$ values obtained from magnetization data. On the other hand, the $\Delta \text{RCP}_{\text{exp}}$ parameters increase with magnetic field, and consequently, pressure increase. We think that this result is a strong evidence of the BCE presence in composite under magnetic field which cannot be detected in $M(T, H)$ measurements. Thus, the total caloric effect in LPM-PT can be considered as the sum of MCE and BCE generated by intrinsic pressure appeared under magnetic field in composite.

We carried out also measurements of ΔT_{AD} using simultaneously magnetic (5 kOe) and electric (2 kV/cm) fields, to make sure that contribution of ECE or piezoelectric effect in PT component initiated by pressure resulted from thermal expansion and magnetostrictive effects discussed above is absent. Experiments were performed in an adiabatic calorimeter. No any detectable difference between the values of $\Delta T_{\text{AD}}(H)$ and $\Delta T_{\text{AD}}(H, E)$ was observed.

It is interesting to consider the changes of some peculiar temperatures under magnetic field in composite compared to those in LPM ceramics. Very often, the inflection point in the $M-T$ curve, i.e., the temperature associated with the minimum value of the $(\partial M/\partial T)_H$ derivative, is defined as the magnetic transformation temperature T_0 (Curie temperature).^{23,24} But as seen from (1) and (2), it is true only for temperature associated with the maximum values of extensive and intensive CE. In accordance with the thermodynamic theory,²⁹ a more correct T_0 is connected with the minimum value of the $(\partial M^2/\partial T)_H$ derivative. Indeed, the entropy ΔS of the

TABLE I. Comparison of $\text{RCP}(T)$ and $\text{RCP}(S)$ for LPM and LPM-PT at $H = 5$ kOe. exp – data obtained analyzing $\Delta T_{\text{AD}}(H, T)$; calc – results of $M(T, H)$ analysis.

Material	$\text{RCP}(T)$, K^2		$\text{RCP}(S)$, J/kg	
	exp	calc	exp	calc
LPM	9.4	12.7	13.7	18.6
LPM-PT	10.8	12.4	15.1	17.7

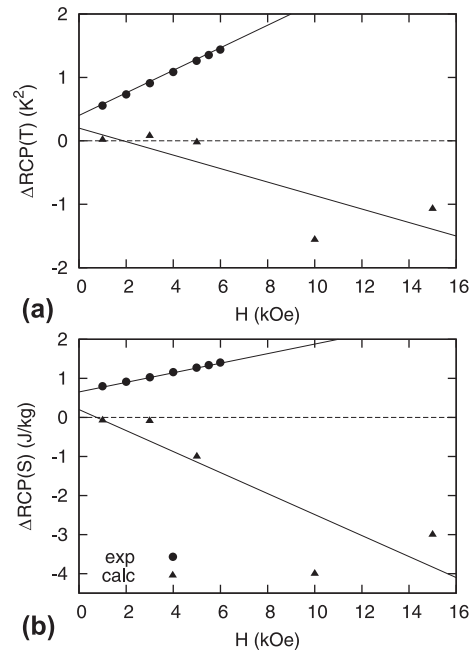


FIG. 4. Field dependences of differences between measured and calculated $\text{RCP}(T)$ (a) as well as $\text{RCP}(S)$ (b) for LPM-PT and LPM.

phase transition is proportional to the square of the order parameter (magnetization M in our case),²⁹

$$-\Delta S = (\partial A/\partial T)M^2 = A_T M^2 \quad (8)$$

where $A = A_T(T - T_0)$ is one of the coefficients of thermodynamic potential,

$$\Phi = \Phi_0 + \Delta\Phi = AM^2 + BM^4 - MH \quad (9)$$

So the inflection points of the $M^2(T)$ and the excess entropy associated with the maximum value of the heat capacity are coincided.

In Fig. 5, the field behavior of two temperatures, considered from different points of view as the phase transition temperatures, and temperature associated with the maximum $\Delta T_{\text{AD}}^{\text{max}}$ value for LPM and LPM-PT is presented. The tendency of change in peculiar temperatures is the same for both samples, i.e., all temperatures increase with elevation in the field. The values of $dT_0^{(dM/dT)}/dH$ and $dT_0^{(\Delta T_{\text{AD}}^{\text{max}})}/dH$ (K/kOe) are rather

close to LPM (0.63 and 0.45) and LPM-PT (0.54 and 0.51). At the same time, the phase transition temperature change in both materials under magnetic field $dT_0^{(dM^2/dT)}/dH(\text{K/kOe})$ is characterized by rather

strong difference 0.07–LPM and 0.25–LPM-PT. From our point of view, the $dT_0^{(dM^2/dT)}/dH$ value in composite can be considered as the sum of the real T_0 shift under magnetic field characteristic for LPM and additional shift under pressure discussed above.

Isothermal $M-H$ curves were measured at various temperatures in the vicinity of ferromagnetic phase transition in LPM and LPM-PT [Figs. 6(a) and 6(b)]. On the ground of these data and using (2), we evaluated ΔT_{AD} values in materials under study. A good agreement was found between the intensive MCE obtained from the analysis of $M(T)_{H=\text{const}}$ and $M(H)_{T=\text{const}}$ dependences.

The $M(H)$ data were also analyzed in the framework of magnetic equation of state obtained from (9) at the equilibrium condition $\partial\Phi/\partial M = 0$

$$H/M = 2A + 4BM^2 \quad (10)$$

A positive slope of the H/M versus M^2 curves in the complete M^2 range [Figs. 6(c) and 6(d)] coincides with a second-order phase transition in both LPM and LPM-PT. The $H/M(M^2)$ dependencies for LPM and LPM-PT are linear. The linear parts of these curves were fitted with a linear least-squares program. This allowed us to determine the temperature behavior of the A and B coefficients in (10). As seen from Figs. 7(a) and 7(c), both parameters depend on temperature almost linearly. Thus, the A_T coefficient ($\text{erg cm}^{-3} \text{K}^{-1}$) is really constant in accordance with the thermodynamic theory²⁸ and is equal to 38.2 (LPM) and 36.8 (LPM-PT). On the other hand, the B coefficient changes below a phase transition

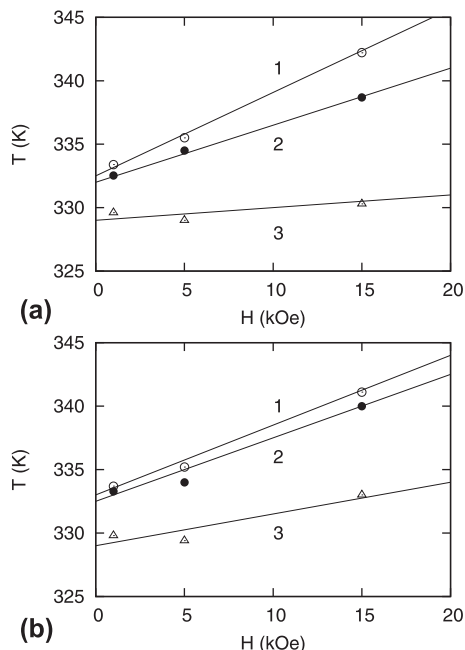


FIG. 5. Field dependences of peculiar temperatures for LPM (a) and LPM-PT (b). 1 – Temperature of the maximum value of $\Delta T_{AD}^{\text{max}}$; 2, 3 – Temperatures of the minimum values of $(\partial M/\partial T)_H$ and $(\partial M^2/\partial T)_H$, respectively.

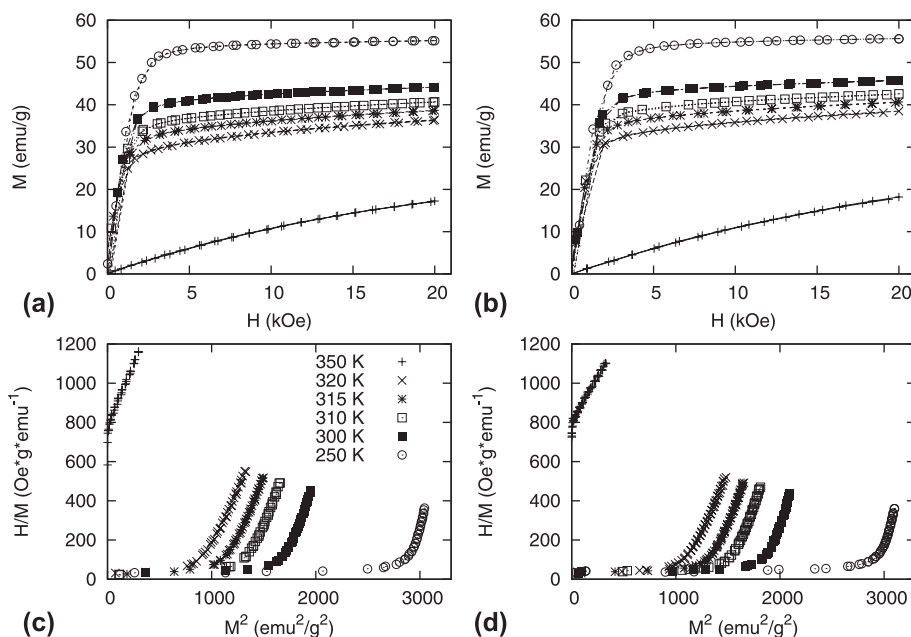


FIG. 6. Field dependences of isothermal magnetization at different temperatures for LPM (a) and LPM-PT (b). H/M versus M^2 curves of isotherms for LPM (c) and LPM-PT (d).

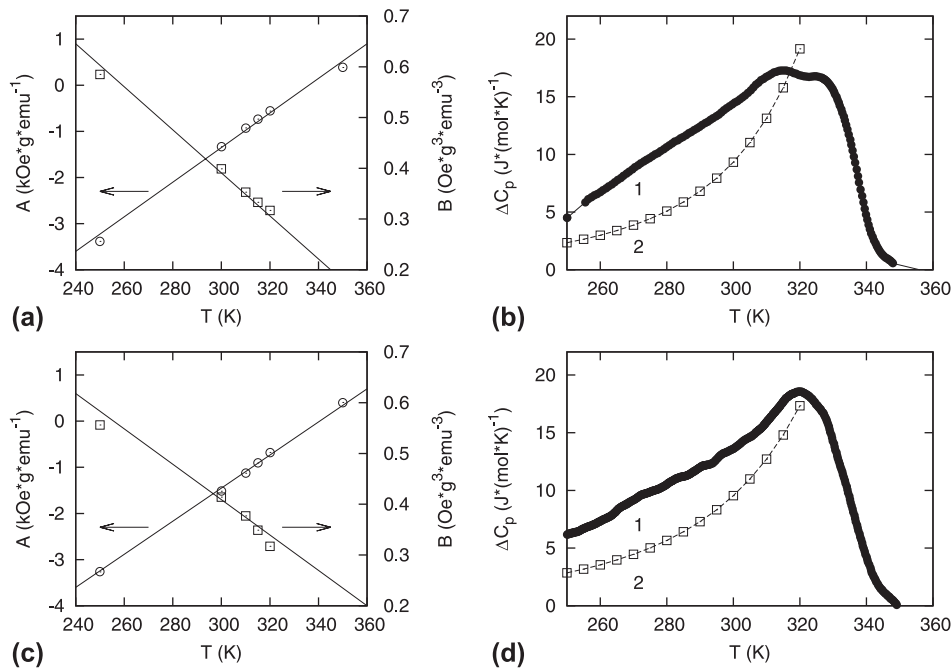


FIG. 7. A and B coefficients versus temperature for LPM (a) and LPM-PT (c). Temperature behavior of excess heat capacity for LPM (b) and LPM-PT (d) measured (1) and calculated (2) using Eq. (12).

point rather strong and can be presented as a linear function of temperature $B = B_T(T - T^*)$ with B_T (erg g cm⁻⁶ K⁻¹) equal to -3.9×10^{-3} and -3.2×10^{-3} for LPM and LPM-PT, respectively. The T^* temperature, where $B = 0$, is 402 K for LPM and 423 K for LPM-PT. The difference in B_T values for composite and LPM ceramics is connected with different closeness of phase transition to the tricritical point discussed above.

Information on the temperature of the second-order phase transition can be obtained from the condition $A_T(T - T_0) = 0$. The T_0 values for both LPM and LPM-PT were found to be equal to 336.2 and 338.7 K, respectively. On the one hand, these temperatures are higher than peculiar temperatures considered above (Fig. 5). On the other, they coincide rather well with temperatures of the maximum values of derivative ($d\Delta C_p/dT$): 337.9 ± 1.5 K (LPM) and 337.5 ± 1.5 K (LPM-PT). The latter temperatures can be considered as the temperatures of the heat capacity jump smeared in ceramic samples.

Expressions for excess entropy as well as heat capacity can be obtained by analysis of thermodynamic potential (9) with two temperature-dependent coefficients, A and B

$$-\Delta S = A_T M^2 + B_T M^4, \quad (11)$$

$$\Delta C_p = -T(A_T^2/2B_T) \left[(T^* - T_0)^2 / (T - T^*)^3 \right]. \quad (12)$$

Figures 7(b) and 7(d) demonstrate that the ΔC_p value is strongly temperature dependent and in ferromagnetic

phase is lower compared to the value determined from experimental data on $C_p(T)$. The different behavior of experimental and calculated excess heat capacity is not strange and can be explained taking into account that Eqs. (11) and (12) are valid for single crystals and calorimetric experiments were performed on ceramic samples. As it was discussed above, phase transitions in ceramic materials are smeared.

IV. CONCLUSION

The study of the temperature and magnetic field dependencies of magnetization was carried out on LPM ceramics and 0.85LPM-0.15PT composite.

It was found that the second-order transformation between para- and ferromagnetic phases in LPM shifts to the tricritical point in LPM-PT composite which leads to the increase of intensive CE. Such an effect and the results of comparison of the RCP at this phase transition determined from the data obtained by the direct and indirect measurements allow us to suppose the important role of intrinsic pressure in composite resulted from elastic interaction between grains of LPM and PT components. Simultaneous measurements on composite under magnetic and electric fields did not show any additional temperature change associated with ECE or IMEC.

The magnetic equation of state was analyzed to determine the coefficients of the thermodynamic potential. A good agreement between the calculated and experimentally measured²¹ anomalous heat capacity was found.

The investigations performed show that volumetric ferroelectric–ferromagnetic composites can be considered as multiferroic materials promising not only to realize multicaloric effects but also to produce additional temperature (or entropy) change because of intrinsic pressure.

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REFERENCES

1. M. Tishin and Y. Spichkin: *The Magnetocaloric Effect and its Application* (Institute of Physics Publishing, Bristol and Philadelphia, 2003), p. 475.
2. A. Planes, L. Manosa, and M. Acet: Magnetocaloric effect and its relation to shape-memory properties in ferromagnetic Heusler alloys. *J. Phys.: Condens. Matter* **21**, 233201(2009).
3. Z. Wei, A. Chak-Tong, and D. You-Wei: Review of magnetocaloric effect in perovskite-type oxides. *Chin. Phys. B* **22**, 057501 (2013).
4. J.F. Scott: Electrocaloric materials. *Annu. Rev. Mater. Res.* **41**, 229 (2011).
5. M. Valant: Electrocaloric materials for future solid-state refrigeration technologies. *Prog. Mater. Sci.* **57**, 980 (2012).
6. S-G. Lu and Q. Zhang: Large electrocaloric effect in relaxor ferroelectrics. *J. Adv. Dielectr.* **2**, 1230011 (2012).
7. T. Strässle and A. Furrer: Cooling by adiabatic (de)pressurization – The barocaloric effect. *High Pressure Res.* **17**, 325 (2000).
8. M.V. Gorev, I.N. Flerov, E.V. Bogdanov, V.N. Voronov, and N.M. Laptash: Barocaloric effect near the structural phase transition in the $\text{Rb}_2\text{KTiOF}_5$ oxyfluoride. *Phys. Solid State* **52**, 377 (2010).
9. E.A. Mikhaleva, I.N. Flerov, V.S. Bondarev, M.V. Gorev, A.D. Vasiliev, and T.N. Davydova: Phase transitions and caloric effects in ferroelectric solid solutions of ammonium and rubidium hydrosulfates. *Phys. Solid State* **53**, 510 (2011).
10. I. Flerov, M. Gorev, A. Tressaud, and N. Laptash: Perovskite-like fluorides and oxyfluorides: Phase transitions and caloric effects. *Crystallogr. Rep.* **56**, 9 (2011).
11. M.P. Annaorazov, S.A. Nikitin, A.L. Tyurin, K.A. Asatryan, and A.K. Dovletov: Anomalously high entropy change in FeRh alloy. *J. Appl. Phys.* **79**, 1689 (1996).
12. L. Manosa, D. Gonzalez-Alonso, A. Planes, E. Bonnot, M. Barrio, J.L. Tamarit, S. Aksoy, and M. Acet: Giant solid-state barocaloric effect in the Ni-Mn-In magnetic shape-memory alloy. *Nat. Mater.* **9**, 478 (2010).
13. P.O. Castillo-Villa, L. Mañosa, A. Planes, D.E. Soto-Parra, J.L. Sánchez-Llamazares, H. Flores-Zúñiga, and C. Frontera: Elastocaloric and magnetocaloric effects in Ni-Mn-Sn(Cu) shape-memory alloy. *J. Appl. Phys.* **113**, 053506 (2013).
14. K.A. Gschneidner, Jr., V.K. Pecharsky, A.O. Pecharsky, V.V. Ivchenko, and E.M. Levin: The nonpareil $\text{R}_5(\text{Si}_x\text{Ge}_{1-x})_4$ phases. *J. Alloys Compd.* **303–304**, 214 (2000).
15. N.A. de Oliveira: Giant magnetocaloric and barocaloric effects in $\text{R}_5\text{Si}_2\text{Ge}_2$ (R = Tb, Gd). *J. Appl. Phys.* **113**, 033910 (2013).
16. E. Mikhaleva, I. Flerov, M. Gorev, M. Molokeev, A. Cherepakhin, A. Kartashev, N. Mikhashenok, and K. Sablina: Caloric characteristics of PbTiO_3 in the temperature range of the ferroelectric phase transition. *Phys. Solid State* **54**, 1832 (2012).
17. M.M. Vopson: The multicaloric effect in multiferroic materials. *Solid State Commun.* **152**, 2067 (2012).
18. S. Lisenkov, B.K. Mani, C-M. Chang, J. Almand, and I. Ponomareva: Multicaloric effect in ferroelectric PbTiO_3 from first principles. *Phys. Rev. B* **87**, 224101 (2013).
19. C. Binek and V. Burobina: Near-room-temperature refrigeration through voltage-controlled entropy change in multiferroics. *Appl. Phys. Lett.* **102**, 031915 (2013).
20. V. Kartashev, E.A. Mikhaleva, M.V. Gorev, E.V. Bogdanov, A.V. Cherepakhin, K.A. Sablina, N.V. Mikhashonok, I.N. Flerov, and N.V. Volkov: Thermal properties, magneto- and baro-caloric effects in $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ single crystal. *J. Appl. Phys.* **113**, 073901 (2013).
21. E. Mikhaleva, I. Flerov, A. Kartashev, M. Gorev, A. Cherepakhin, K. Sablina, N. Mikhashenok, N. Volkov, and A. Shabanov: Caloric effects and phase transitions in ferromagnetic–ferroelectric composites $x\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3-(1-x)\text{PbTiO}_3$. *J. Mater. Res.* **28**, 3322 (2013).
22. E.G. Fesenko, V.G. Gavriyachenko, and E.V. Zaroquentsev: Segnetoelektricheskie svoystva monokristallov titanata svinca. *Izv. Akad. Nauk SSSR, Ser. Fiz.* **34**, 2541 (1970).
23. N. Volkov, G. Petrakovskii, P. Boeni, E. Clementyev, K. Patrin, K. Sablina, D. Velikanov, and A. Vasiliev: Intrinsic magnetic inhomogeneity of Eu substituted $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ single crystals. *J. Magn. Magn. Mater.* **309**, 1 (2007).
24. J. Gutiérrez, J.R. Fernández, J.M. Barandiarán, I. Orúe, and L. Righi: Magnetocaloric effect in $(\text{La}_{0.55}\text{Bi}_{0.15})\text{Ca}_{0.3}\text{MnO}_3$ perovskites. *Sens. Actuators, A* **142**, 549 (2008).
25. Y. Sun, J. Kamarad, Z. Arnold, Z. Kou, and Z. Cheng: Tuning of magnetocaloric effect in a $\text{La}_{0.69}\text{Ca}_{0.31}\text{MnO}_3$ single crystal by pressure. *Appl. Phys. Lett.* **88**, 102505 (2006).
26. S.G. Min, K.S. Kim, S.C. Yu, H.S. Suh, and S.W. Lee: Magnetocaloric properties of $\text{La}_{1-x}\text{Pb}_x\text{MnO}_3$ ($x = 0:1; 0:2; 0:3$) compounds. *IEEE Trans. Magn.* **41**, 2760 (2005).
27. D.L. Rocco, R.A. Silva, A.M.G. Carvalho, A.A. Coelho, J.P. Andreetta, and S. Gama: Magnetocaloric effect of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ compound under pressure. *J. Appl. Phys.* **97**, 10M317 (2005).
28. V.K. Pecharsky and K.A. Gschneidner, Jr.: Magnetocaloric effect from indirect measurements: Magnetization and heat capacity. *J. Appl. Phys.* **86**, 565 (1999).
29. K.S. Alexandrov and I.N. Flerov: The regions of applicability of the thermodynamic theory of structural phase transitions close to the tricritical point. *Sov. Phys. Solid State* **21**, 195 (1979).