

# Effect of Sequential Heat Impacts on the Formation of a Stable State of the $x\text{LPM}-(1-x)\text{PT}$ Multiferroic Composites

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**Abstract**—The effect of thermal cycling and sintering temperature on the chemical and thermodynamic stability of the bulk multiferroic  $x\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3-(1-x)\text{PbTiO}_3$  quasi-ceramic and ceramic composites has been experimentally investigated. It is shown that the limiting temperature of the long-term sample firing should not exceed 1070 K. It has been found that sintering at this temperature and/or short-term exposure of the samples at higher temperatures (up to 1220 K) significantly increase the sample compactness, stabilize the thermal expansion, and enhance the quality of the composites. It has been established that the component grain integrity is violated by shrinkage of the samples and a sharp change in their volume during the phase transition of a ferroelectric component.

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## 1. INTRODUCTION

In recent years, there has been a keen interest in multiferroic materials, where the double or even triple different ordering types can exist: ferromagnetic, ferroelectric, and ferroelastic [1–6]. This interest is evoked, in particular, by the possibility of creating functional elements for micro- and nanoelectronics on the basis of multiferroics, the properties of which can be controlled via combining different external fields. However, of greatest interest seem to be multiferroics, which are characterized by a fairly strong direct interaction between different order parameters, which leads to the magnetoelectric, magnetoelastic, and electroelastic effects [7–10]. In this case, different physical effects can be controlled by one field. The interaction of the electric, magnetic, and elastic subsystems in one material is also interesting for application in designing solid-state cooling agents with the multicaloric properties related to the temperature/entropy variation in several subsystems under the action of one field. The multiferroic and multicaloric properties of single-phase materials, which are caused by the direct interaction between the order parameters of different subsystems, are usually insignificant [6, 11]. These effects in composite materials can be enhanced by creating a reliable mechanical contact between components with the electrical, magnetic, and elastic order parameters [6, 12, 13]. When a composite is placed in an electric or magnetic field, the

striction and piezoelectric properties of its components occur, which induce stresses at the contact boundaries of different ferroic materials [4]. A significant contribution to these stresses can also be made by the difference between the thermal expansion coefficients  $\alpha$  (TECs) of components, which is especially pronounced in the region of their characteristic phase transitions.

The bulk (mixed) composites have at least two advantages over the layered (bilayer/multilayer film or bulk) composite materials. First, the mechanical interaction between different grains is mainly spatial and the difference between coefficients  $\alpha$  is averaged over the composite volume. As a result, the induced stresses can be considered to be similar to hydrostatic. In layered systems, the tensile or compressive stresses arise in the plane of the contact between component layers and are two-dimensional, which causes a stress gradient across the composite sample thickness. Second, bulk composites are relatively easy to fabricate using standard ceramic technology. However, a very important problem is to choose the optimal temperature of firing (sintering) the composite materials. On the one hand, this temperature should help obtain compact samples, which will strengthen the mechanical interaction between components. On the other hand, at this temperature, it is necessary to prevent the formation of solid solutions and chemical decomposition (degradation) of components; otherwise, they will inevitably lead to a sharp change in the composite

properties. This is especially important for forming composite materials with essentially different component melting points.

The recent studies on the bulk multiferroic composites based on  $\text{PbTiO}_3$  (PT) and  $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$  (LPM), which undergo the ferroelectric and ferromagnetic phase transitions, respectively, have shown the possibility of enhancing the caloric efficiency of these materials via the stresses induced at the LPM and PT grain contact boundaries in a sample placed in a magnetic or electric field [13]. This results in the simultaneous implementation of the paired caloric effects in the  $x\text{LPM}-(1-x)\text{PT}$  composites, including (i) the magnetocaloric effect (MCE) and barocaloric effect (BCE) in the region of ferromagnetic transformation and (ii) the electrocaloric effect (ECE) and BCE at the ferroelectric phase transition. It was established that in the region of phase transitions at the relatively low magnetic ( $H = 5$  kOe) and electric ( $E \leq 1$  kV/cm) field strengths, the BCE value can attain about (20–40)% of the MCE and ECE value. The composites were sintered at 1070 K in air [13]. The ceramic sample compactness changed within 75–90% upon variation in the LPM concentration from 18 to 85%. The question about the possible increase in the sintering temperature for enhancing the  $x\text{LPM}-(1-x)\text{PT}$  ceramic sample compactness remained unanswered.

In this work, we experimentally studied the effect of thermal cycling and firing temperature regimes on the formation of stable thermal properties of the  $x\text{LPM}-(1-x)\text{PT}$  multiferroic ceramic composites and their chemical stability.

## 2. EXPERIMENTAL

The  $x\text{LPM}-(1-x)\text{PT}$  multiferroic composites were investigated using samples of the two types: (i) quasi-ceramic samples prepared by grinding a mixture of initial components and pressing without binding materials under a pressure of  $\sim 0.1$  GPa at room temperature without subsequent heat treatment and (ii) classical ceramic samples sintered in air for four hours at firing temperatures from 1070 to 1220 K. The mass ratios of the initial components were 0.15 : 0.85, 0.40 : 0.60, and 0.60 : 0.40.

The structural characterization of the composites samples and refinement of the component concentrations were performed on a Bruker D8 ADVANCE X-ray powder diffractometer ( $\text{CuK}_\alpha$  radiation).

The composite surface morphology and component grain sizes were examined using a Hitachi TM3000 scanning electron microscope (SEM) (Hitachi, Japan).

In the investigated composites, the anomalies of the thermal properties of lead titanate related to the first-order phase transition close to the tricritical point are the most pronounced [14]. The second-order fer-

romagnetic transformation in LPM is accompanied by a small  $\alpha$  anomaly [15], the study of which in composites with the high PT concentration is less informative. Therefore, we focused upon studying the phase transition region in the PT component.

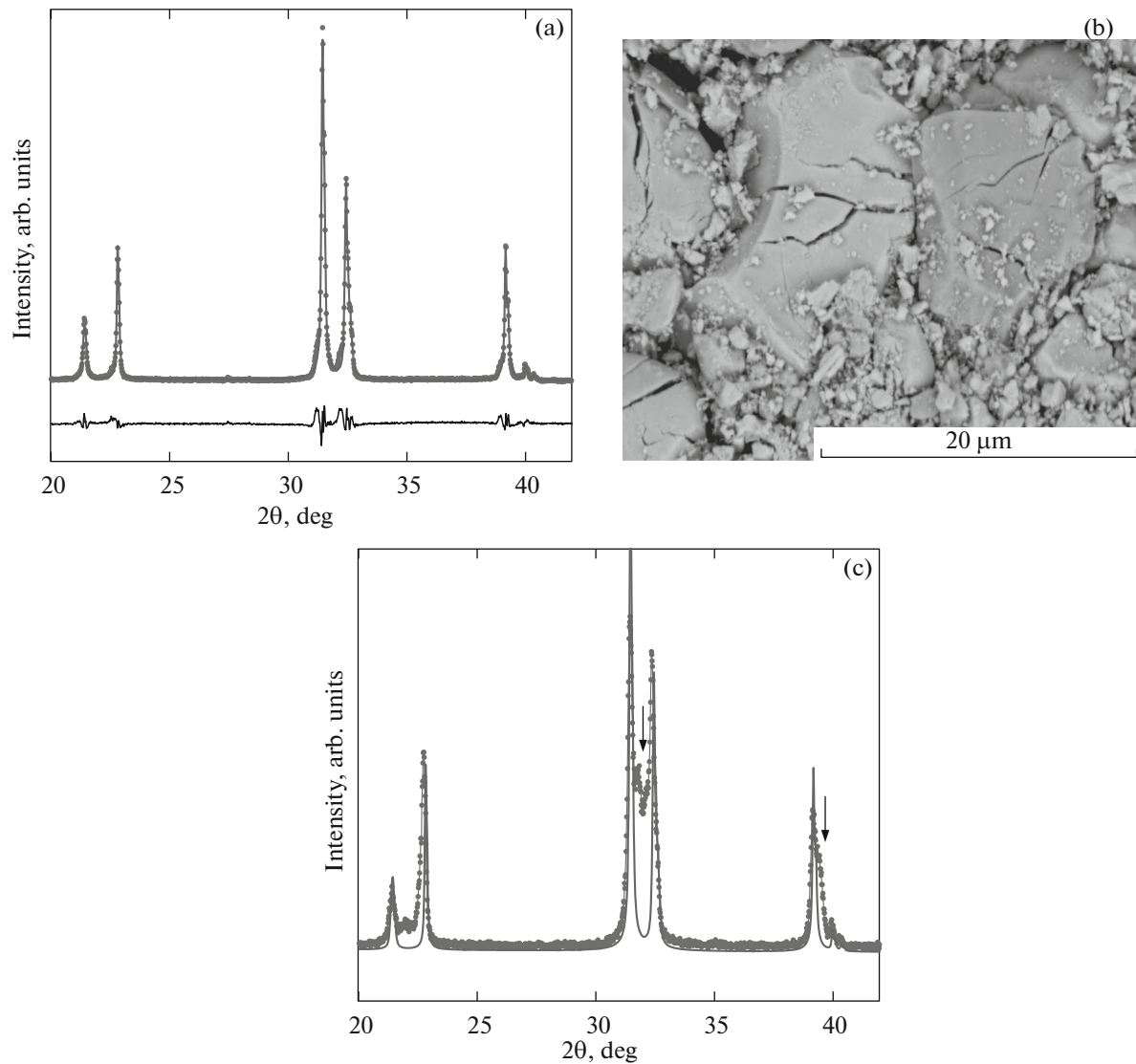
The dilatometric method was chosen as a main tool, since it allowed us to obtain information both on the change in the linear sample size after shrinkage of the composite ceramics during sintering and on the effect of thermal cycling on the temperature behavior of thermal expansion.

The temperature dependences of the linear strain  $\Delta L/L_0$  and linear TEC  $\alpha$  were studied on a NETZSCH DIL-402C induction dilatometer. The measurements were performed in the dry helium gas flow using tableted samples with a diameter of 8 mm and a thickness of 1 mm. The sample heating/cooling rate was  $3 \text{ K min}^{-1}$ . A fused quartz reference was used for calibration and taking into account the expansion of the measuring system.

## 3. RESULTS AND DISCUSSION

Figure 1a presents an X-ray diffraction pattern of the composite with  $x = 0.18$ , which is typical also of the other investigated composites with the intensity redistribution of the observed structural reflections corresponding to the rhombohedral (LPM) and tetragonal (PT) phases upon variation in the  $x$  value. The refinement of the component concentrations yielded mass ratios of 0.18 : 0.82, 0.32 : 0.68, and 0.69 : 0.31. No traces of impurities or foreign phases were found in the X-ray diffraction patterns of the composites, which is indicative of the absence of forming solid solutions and mutual diffusion of the components.

Figure 1b shows a SEM image of the sample after heat treatment. It can be seen that the grains of both components with a size of no larger than 10–15  $\mu\text{m}$  contain cracks (the PT grains are brighter). At the same time, the study of the samples before sintering showed that cracking was only typical of the PT grains, which can be attributed, in particular, to the strong volume change during the ferroelectric phase transition at  $T_0^{\text{FE}} = 763 \text{ K}$  [14], through which the sample inevitably passes during cooling after the high-temperature synthesis. The possible reasons for the LPM grain cracking in the composite are discussed below by analyzing the thermal expansion of the composites with different  $x$  values. However, this phenomenon can be attributed in advance to the significant difference between the coefficients  $\alpha$  of the components [14, 15]. At room temperature, the  $\alpha$  value of LPM is  $\alpha > 0$ ; with increasing temperature, it slowly grows. Lead titanate is characterized by the negative thermal expansion from  $\sim 100 \text{ K}$  to  $T_0^{\text{FE}}$ , where the  $\alpha$  value grows



**Fig. 1.** Results of investigations of the 0.18LPM–0.82PT ceramic composite: (a) refinement of the structural model, (b) SEM image of the sample surface, and (c) X-ray diffraction pattern of the sample sintered at  $T = 1120$  K. Arrows show unidentified reflections.

very fast to positive values of  $(3.0 \pm 0.3) \times 10^{-5} \text{ K}^{-1}$ , which are similar to  $\alpha = (3.8 \pm 0.3) \times 10^{-5} \text{ K}^{-1}$  for LPM.

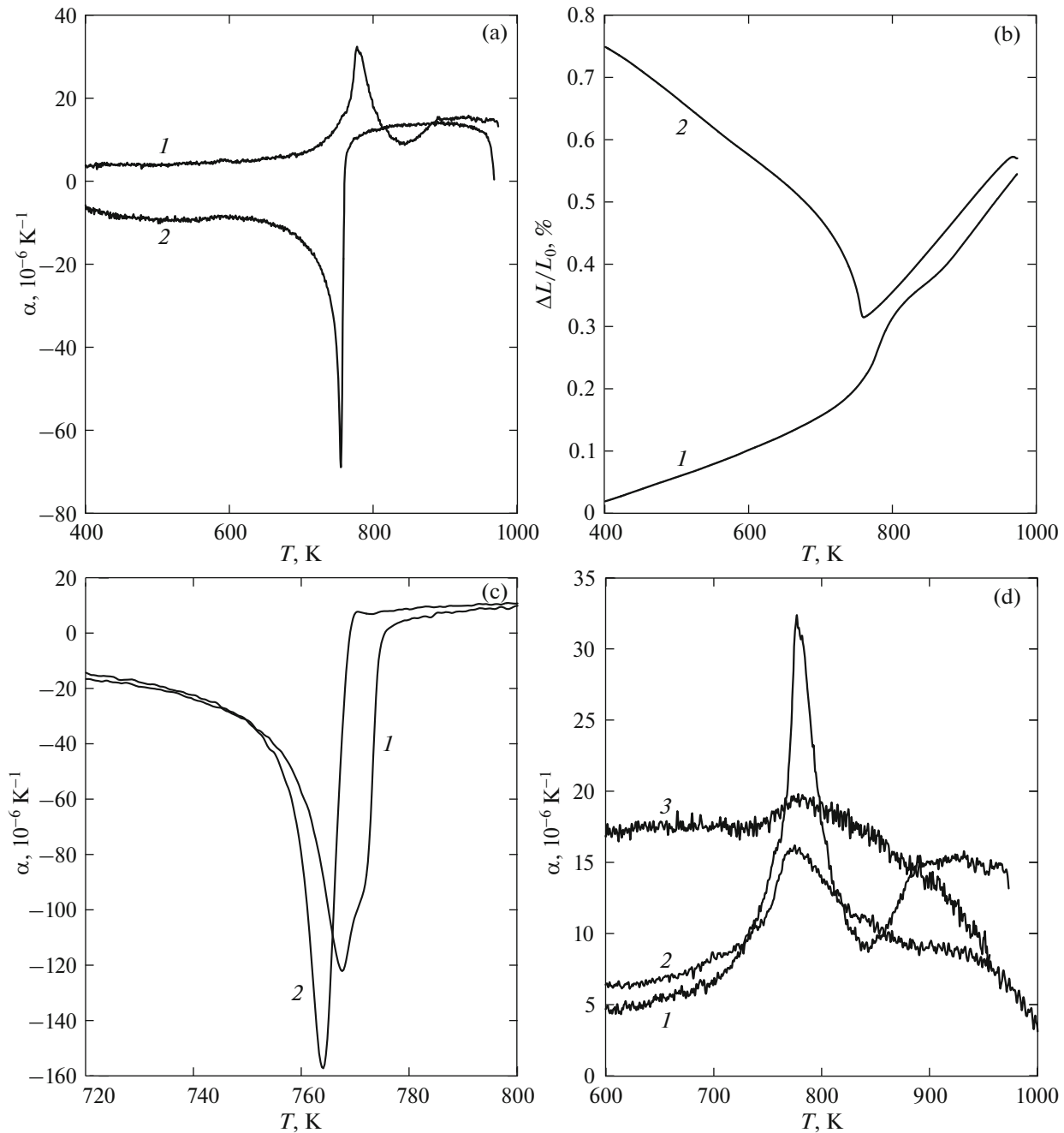
At the first stage, the TEC of the quasi-ceramics with  $x = 0.18$  was studied. The measurements were performed during the primary sample heating from 300 to 970 K almost without exposure at high temperature (Fig. 2a).

A number of the features, unexpected at first glance, were observed in the  $\alpha(T)$  dependences. First, it was found that  $\alpha > 0$  over the entire temperature range, despite the predominance of lead titanate in the composite, for which we have  $\alpha < 0$ , at least at  $T < T_0^{\text{FE}}$ . Second, instead of the expected negative thermal

expansion anomaly at  $T_0^{\text{FE}}$  in bulk PT, we observed a significant positive anomaly with a maximum temperature of  $\sim 777$  K, which is slightly higher than the ferroelectric phase transition temperature. Figure 2b illustrates the behavior of the quasi-ceramic strain during the first heating, which shows that the linear sample size increased by 0.1%.

At temperatures above  $T_0^{\text{FE}}$ , up to 970 K, the  $\alpha$  value is similar to the value of  $\alpha = +(3.0 \pm 0.3) \times 10^{-5} \text{ K}^{-1}$  typical of lead titanate [14].

The TEC measurements in the cooling mode were performed after expose of the sample at 970 K for several minutes. A negative anomaly with the  $\alpha(T)$  minimum was found at  $T_0^{\text{FE}\downarrow} = 753.2$  K (Fig. 2a), which is



**Fig. 2.** (a, b) Temperature dependences of the thermal expansion coefficient  $\alpha$  and strain  $\Delta L/L_0$  of the  $x\text{LPM}-(1-x)\text{PT}$  composites: (1) first heating and (2) subsequent cooling of the 0.18LPM–0.82PT quasi-ceramics. (c) Temperature behavior of  $\alpha$  (1) before and (2) after sintering of the 0.18LPM–0.82PT composite. (d) Effect of the component concentration ratios on the temperature dependences of the quasi-ceramics during the first heating.  $x =$  (1) 0.18, (2) 0.32, and (3) 0.69.

slightly higher than  $T_0^{\text{FE}\downarrow} = 752$  K observed in pure bulk PT [14]. In the paraelectric phase, the relative strain decreases to the temperature  $T_0^{\text{FE}\downarrow}$  below which the  $\Delta L/L_0$  value growth to 0.75% after attaining 400 K (Fig. 2b). Thus, after the first cycle of heating–cooling of the quasi-ceramics (without sintering), the composite compactness noticeably degraded. As a result of

further thermocycling, the  $\alpha$  anomaly in the quasi-ceramics is stabilized at the minimum value ( $\alpha_{\min} \approx 1.2 \times 10^{-4} \text{ K}^{-1}$ ) and the transition temperature:  $T_0^{\text{FE}\uparrow} = 768$  K and  $T_0^{\text{FE}\downarrow} = 753$  K. Above  $T_0^{\text{FE}\uparrow}$ , the TEC of the PT component rapidly grows from  $-1.2 \times 10^{-5} \text{ K}^{-1}$  to  $0 \text{ K}^{-1}$  in the narrow temperature range from 768 to 775 K.

At the next stage, the investigated quasi-ceramic sample with  $x = 0.18$  was sintered for 4 h at 1070 K in air and slowly cooled ( $dT/d\tau \approx 0.5 \text{ K min}^{-1}$ ) to room temperature. As a result of firing, already upon the first heating of the sample subjected to the heat treatment, the negative TEC anomaly was only detected, which is related to the phase transition in the PT component (Fig. 2c). As expected, due to the low ferromagnetic component concentration, we have  $\alpha < 0$  for the composite in a wide temperature range below the transition temperature. In the three sequential series of measurements in the composite heating mode, the transition temperature is reproduced well ( $T_0^{\text{FE}\uparrow} = 764.0 \pm 0.1 \text{ K}$ ) and the  $\alpha$  minimum appears to be deeper by  $\sim 30\%$  as compared with the value for quasi-ceramics. It is worth noting that above  $T_0^{\text{FE}\uparrow}$ , i.e., in the paraelectric phase, the coefficient  $\alpha$  of the ceramic sample attains a regular value of  $(3.0 \pm 0.3) \times 10^{-5} \text{ K}^{-1}$  in a narrower temperature range than in the case of quasi-ceramics. This is indicative of the lower transition spreading due to the better quality of the ceramic composite after sintering, which can also be considered as an annealing process.

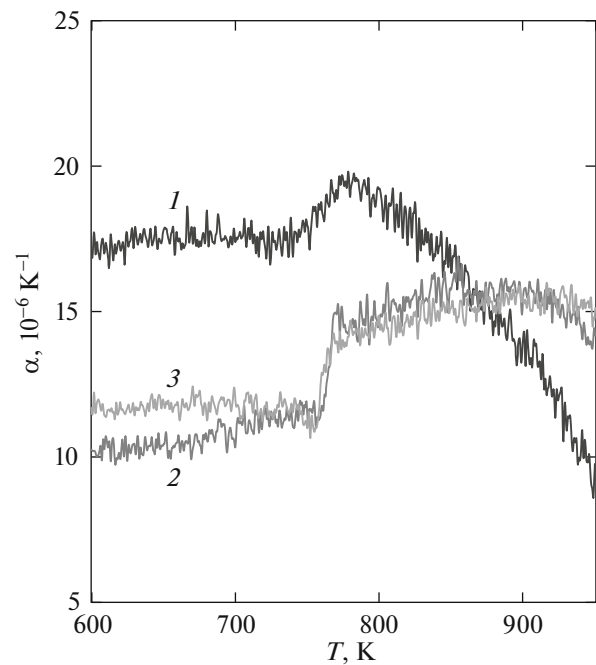
In addition, we examined the  $\alpha(T)$  behavior during the first heating of the as-synthesized quasi-ceramic samples with the higher LPM component contents ( $x = 0.32$  and  $0.69$ ). We observed quite satisfactory qualitative agreement between these data and the behavior of the thermal expansion of the composite with  $x = 0.18$  (Fig. 2d). It can be seen that the increase in the LPM concentration leads to

(i) an increase in the TEC in both composite phases, which is positive over the entire temperature range and

(ii) a significant decrease in the values of positive anomalies upon slight variation in the maximum temperature ( $776.4 \pm 0.5 \text{ K}$ ).

These facts unambiguously show that the positive TEC anomaly is related to the change in the thermal expansion of the PT component.

For the quasi-ceramic and ceramic composite samples with the high LPM content ( $x = 0.69$ ), the sequential dilatometric investigations were carried out. The results obtained (Fig. 3) are consistent with the observed behavior of the TEC of the composite with  $x = 0.18$ . However, due to the low PT component concentration, the main contribution to the TEC is made by LPM; thus, the coefficient  $\alpha$  remains positive for both samples over the entire temperature range, including the phase transition region. However, the TEC in the ferroelectric phase is noticeably smaller than in the paraelectric phase. The effect of increasing ferromagnetic component concentration on the transition temperature of lead titanate was found to be fairly weak; it decreased by  $\sim 9 \text{ K}$  relative to  $T_0^{\text{FE}\uparrow} = 763.8 \text{ K}$  in the composite with  $x = 0.18$ . Sintering of the composite with  $x = 0.69$  at 1070 K did not

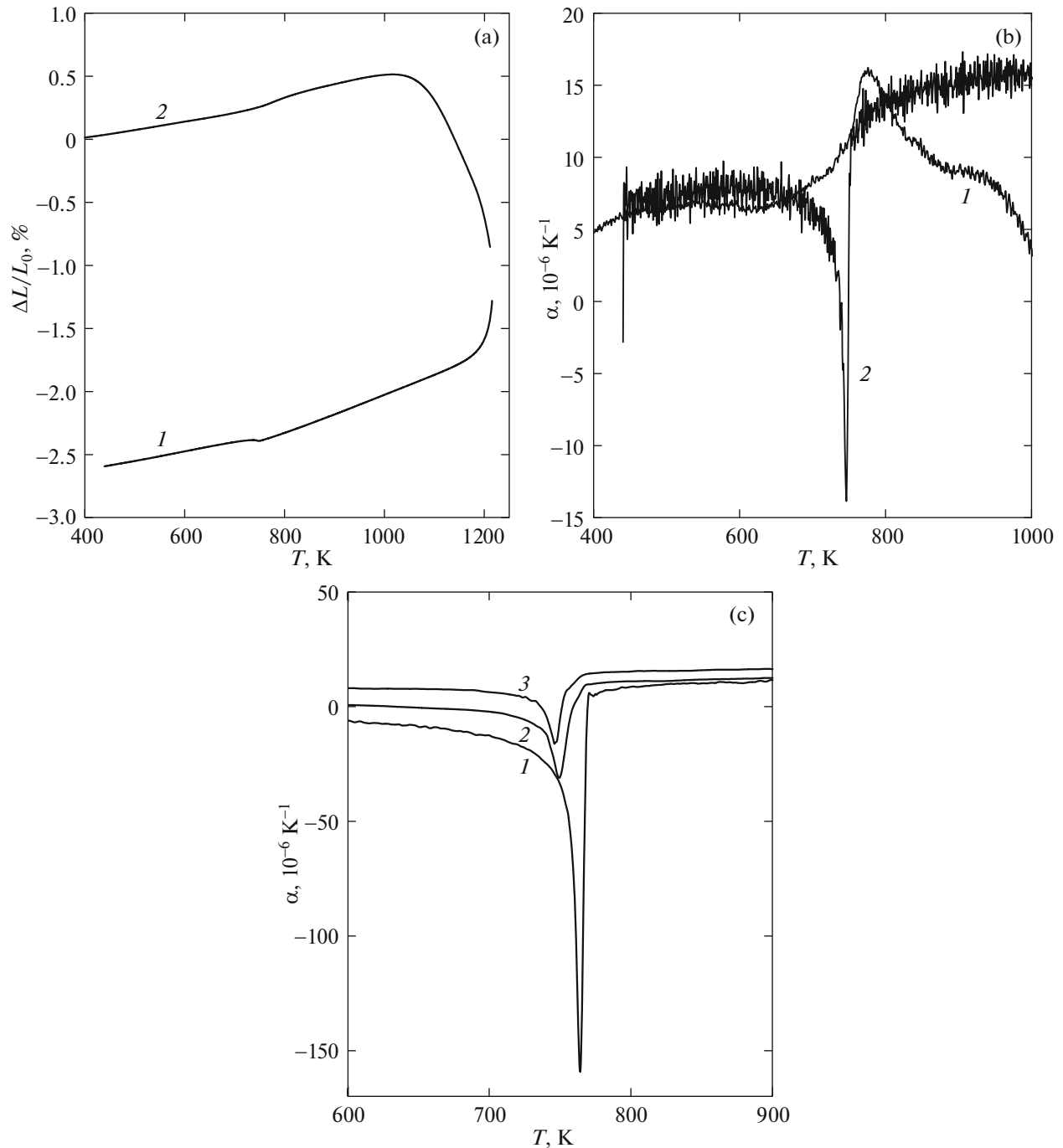


**Fig. 3.** Temperature dependences of the thermal expansion coefficient of the 0.69LPM–0.31PT composite: (1) first and (2) second heating before sintering and (3) heating after sintering at 1070 K.

noticeably modify the  $\alpha(T)$  dependence. Within the measurement error, the data on the unfired sample, sample exposed to a temperature of 1070 K for only a few minutes, and fired sample almost coincide (Fig. 3).

The point to note is the specific features of the TEC behavior during the first heating of the quasi-composites with  $x = 0.32$  and  $0.69$  (Figs. 2d and 3). Both samples are characterized by a rapid significant decrease in the  $\alpha$  value above the maximum temperature, which was not observed when measuring the TEC during the first heating of the composite with  $x = 0.18$  to almost the same temperature (Fig. 2). Moreover, an increase in  $x$  lowers the temperature at which the TEC starts decreasing, indicating a decrease in the composite sizes (shrinkage) and, thus, an increase in the sample compactness. These data suggest that the low compactness of the composite with  $x = 0.18$  (75%) can be caused by the insufficiently high sintering temperature (1070 K) [13]. On the other hand, according to the above X-ray structural data, under these sintering conditions the chemical integrity of the components is reliably preserved.

The question about the possibility of enhancing the compactness of the  $x\text{LPM} - (1 - x)\text{PT}$  composites by increasing the sintering temperature was solved in two stages. First, the dilatometric study of the composite with  $x = 0.32$  was carried out in a wider temperature range, up to 1220 K. As follows from Fig. 4a, during the first heating, the strain increases ( $\alpha > 0$ ) to  $\sim 1000 \text{ K}$ ;



**Fig. 4.** (a) Temperature dependences of strain and thermal expansion coefficient of the quasi-ceramics with  $x = 0.32$  during the first (1) heating–(2) cooling cycle. (b) Sintering temperature dependence of the TEC of the 0.18LPM–0.82PT composite at (1) 1070, (2) 1120, and (3) 1220 K.

then, its growth slows down and a rapid significant decrease in  $\Delta L/L_0$  starts, which is indicative of the change of the  $\alpha$  sign for negative (Fig. 4b).

Since before the  $\alpha(T)$  measurements in the cooling mode the sample was exposed at 1220 K for only a few minutes, we may assume that the ceramics were almost unsintered. On the other hand, heating to this

temperature leads to a decrease in the sample size by  $\sim 1\%$  relative to  $L_0$ , which speaks about the composite shrinkage (Fig. 4a). The subsequent cooling was accompanied by a further decrease in  $\Delta L/L_0$  with the negative TEC anomaly during the ferroelectric transition in the PT component. Moreover, beyond the phase transition region, the  $\alpha$  value was positive. As a

result of the first heating–cooling cycle, the total decrease in the sample size was  $\sim 2.5\%$ . The X-ray diffraction data for the composite with  $x = 0.32$  after the discussed cycle showed no additional reflections in the X-ray diffraction pattern; i.e., during the short-term exposure of the composite at 1220 K, the integrity of its chemical composition did not break, but the composite compactness significantly increased.

The obtained TEC data allowed us to make the following assumptions. As a result of room-temperature pressing under a fairly high pressure (0.1 GPa), the quasi-composite appears clamped; i.e., there are strong positive stresses at the grain contact boundaries. The temperature growth during the first heating reduces the stresses and enhances the quasi-composite size ( $\alpha > 0$ ), especially rapidly at  $T > T_0^{\text{FE}\uparrow}$ . In this case, the intergrain contact degrades and the composite becomes loose (less compact); therefore, the negative  $\alpha(T)$  anomaly typical of PT is not observed (Figs. 2a and 4b).

The spread positive  $\alpha(T)$  anomaly during the first heating is always observed in the temperature range of  $\sim (650\text{--}850)$  K with the maximum slightly higher than the temperature  $T_0^{\text{FE}\uparrow}$  of the transition in the ferroelectric component. Upon cooling below  $T_0^{\text{FE}\downarrow}$ , the PT grain size grows ( $\alpha < 0$ ) and the LPM grains are compressed. This circumstance can be considered as a cause for the grain destruction in both components, which was observed in the SEM experiments.

At the next stage, we studied the stability of the  $x\text{LPM}-(1-x)\text{PT}$  composites against the high firing temperature. Since the anomalous TEC value related to the ferroelectric phase transition is the most pronounced in the ceramics with  $x = 0.18$ , the thermal expansion measurements after the composite sintering for 4 h at temperatures above 1070 K were performed on this sample. The results obtained are shown in Fig. 4c. An increase in the firing temperature to 1120 K led to

- (i) an increase in the negative  $\alpha$  value at temperatures below  $T_0^{\text{FE}}$ ,
- (ii) a sharp decrease (by a factor of about 4) in the negative TEC anomaly related to the phase transition in the ferroelectric component, and
- (iii) a significant decrease in the ferroelectric transition temperature to  $T_0^{\text{FE}\uparrow} = 749$  K as compared with the temperature  $T_0^{\text{FE}\uparrow} = 764$  K observed after firing at 1070 K.

The further increase in the sintering temperature to 1220 K resulted in the further decrease in the temperature  $T_0^{\text{FE}\uparrow}$  by 3 K; the  $\alpha$  values at  $T < T_0^{\text{FE}\uparrow}$  and  $T > T_0^{\text{FE}\uparrow}$  far from the transition and anomalous contribution to the TEC increased and decreased, respectively.

The established experimental facts allowed us to assume with high confidence that an increase in the temperature of sintering of the  $x\text{LPM}-(1-x)\text{PT}$  composites above 1070 K is accompanied by degradation of the ferroelectric component. The X-ray diffraction study of the sample subjected to such heat treatment confirmed this assumption: the X-ray diffraction pattern of the composite with  $x = 0.18$  contained additional unidentified reflections (Fig. 1c).

Thus, thermal cycling leads to the implementation of the thermodynamic equilibrium in the  $x\text{LPM}-(1-x)\text{PT}$  multiferroic composites, which manifests itself in the stable reproduction of the TEC behavior in the ferroelectric phase transition region, and to the enhanced sample compactness. The growth of the composite compactness will undoubtedly lead to an increase in stresses between heterogeneous grains under the action of external fields and, consequently, in the caloric effects (ECE and MCE), due to the additional BCE contribution [13].

It is not excluded that another way of obtaining more compact  $x\text{LPM}-(1-x)\text{PT}$  composites at the same sintering temperature is related to a decrease in the volume of component grains, which can be implemented, e.g., in nanocomposites.

#### 4. CONCLUSIONS

In this work, we studied the dependence of the thermodynamic and chemical stability of the  $x\text{LPM}-(1-x)\text{PT}$  composites via examining the thermal expansion of quasi-ceramic and ceramic samples under different temperature conditions.

The nature of the nonreproducible positive TEC anomaly in the quasi-composites, which was observed during the first heating in the temperature range close to the phase transition region in the ferroelectric component was discussed.

It was shown that the limiting temperature of long-term sintering of the investigated multiferroic composites should be no higher than 1070 K. A further increase in the sintering temperature leads to chemical degradation of the ferroelectric component. However, the short-term exposure of the samples even at a temperature of 1220 K does not violate their chemical integrity and facilitates a significant increase in the compactness.

The reason for the destruction of ferromagnetic and ferroelectric grains during the heating–cooling cycle is related to the rapid growth of the PT grain size upon cooling the composites below  $T_0^{\text{FE}\downarrow}$ , which leads to the compression of LPM grains.

Another way to increase the compactness of the  $x\text{LPM}-(1-x)\text{PT}$  ceramic samples can be related to a decrease in the grain size, e.g., by preparing nanoceramic composites.

Since all the results obtained are only related to the phase transition in the ferroelectric component of the multiferroic composites, they can be extended to designing the composites with a passive nonferroic component possessing the essentially different (large or small) thermal expansion as compared with the active component undergoing a phase transition.

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