Thermal expansion of solid solutions of the Pb(Zr,Ti)O$_3$ system near lead zirconate

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Abstract. Ferroelectric ceramic materials based on the Pb(Zr,Ti)O$_3$ (PZT) system were obtained by two-stage solid-phase synthesis followed by sintering using conventional ceramic technology. On the basis of the studies correlations between the thermal expansion and structural parameters of the investigated solid solutions were established. It was concluded that the obtained data are recommended to be used in the development of devices based on solid solutions with the participation of the PZT system.

1. Introduction

Solid solutions (SS) based on the PZT system, (Pb(Zr,Ti)O$_3$), have excellent piezoelectric properties [1–5], as a result of which they attract great attention of various research groups for use in a wide range of piezoelectric devices (sensors, actuators, transformers, etc.). The rapid development of this instrumental base, as well as the desire for versatility, leads to the fact that the used ferroactive components operate in extreme external conditions, one of which is often temperature. The resulting thermal stresses are the cause of strength fatigue, deterioration of performance and, in some cases, destruction of both the piezoelectric element and the structure of the device as a whole. Due to the fact that thermophysical studies of this system have practically not been carried out, with the exception of several works in which the objects were single compositions of SS from different regions of the phase diagram [6-7], often investigated at room temperature, it seems relevant to study the thermophysical properties of the SS of the system in wide concentration (near one of the extreme components) and temperature ranges, which became the goal of the presented work.

2. Objects and methods of research

The objects of research were SS of composition (1-x)PbZrO$_3$-xPbTiO$_3$ (0.0≤x≤0.35). Samples of SS were obtained by conventional ceramic technology (solid-phase synthesis, sintering without applying pressure). The synthesis of the SS system was carried out in two stages with intermediate grinding and powder granulation. Synthesis modes: temperature of the first calcination $T_1=1140$K, second $T_2=1170$K. Isothermal holding at both temperatures was $t_1=t_2=7$ hours. Selection of the optimum sintering temperature ($T_{\text{sim}}$) as made by choosing from three used sintering temperatures $T_{\text{sim}}$, lying in the range (1470 ... 1530) K. X-ray diffraction study in the range (300 ÷ 750) K was carried out by powder X-ray diffraction on an ADP-1 diffractometer (Bragg - Brentano focusing scheme) using CuK$_\alpha$ radiation.

The experimental samples were made in the form of disks 10 mm in diameter and 2 mm in height. The experimental samples were made in the form of disks 10 mm in diameter and 2 mm in height. The
study of linear thermal expansion (\(\alpha\)) and relative elongation (\(\Delta L/L\)) was carried out in an oxygen atmosphere on a specially designed stand, including a device for checking gage blocks Mikron-02 (Ltd “Firm “TOT”, Yaroslavl, Russia) and digital nanovolmeter Agilent 34401A (Keysight technologies, Malaysia). The temperature in the chamber was controlled using a Varta 703I thermocontroller (Ltd “SPC “VARTA”, St. Petersburg, Russia). The calculation of \(\Delta L/L\) (step \(\Delta T = 1\)K) and the linear coefficient of thermal expansion (\(\alpha\)) were carried out according to the standard method [8]. The heating rate was 1 K/min. At each temperature point, ~ 8–10 strain values were obtained, after which averaging was performed. The error in measuring the coefficient of thermal expansion is no more than 3%.

3. Experimental results and discussion

Figure 1 shows a fragment of the \(x\)-\(T\)-diagram of the system constructed by us in [9]. Here, single oblique shading denotes single-phase regions, single vertical shading denotes an area of fuzzy symmetry, and double shading denotes a region of coexistence of phases or phase states. \(MR_1\) - morphotropic region; \(Pba2\) - space group of the rhombic (\(R\)) phase; \(R3c, R3m\) — space groups of the rhombohedral (\(Rh\)) phase; \(Pm3m\) is the space group of the cubic (\(C\)) phase. At transition to the \(C\)-phase (see Figure. 1), the Curie temperature can be determined. When the content of lead zirconate is \(0.00 \leq x \leq 0.04\), the phase transition belongs to the first kind, for the \(x > 0.04\), the transition is of the second kind.

Figure 2 shows the most typical temperature dependences of the unit cell volume \((V)\), as well as \(\alpha\) and \(\Delta L/L\), for ceramic samples of solid solutions with \(x = 0.0\) (\(a\)), 0.1 (\(b\)), 0.5 (\(c\)), 0.16 (\(d\)), 0.24 (\(e\)), 0.35 (\(f\)). Dependences \(V(T)\) are shown in the graphs (Figure. 2) to show the correlation between changes in the internal structure and macro-responses. An abrupt change in the parameter is evidence in favor of a first-order transition. A smooth change in this value indicates a second-order transition.

![Figure 1. Fragment of x-T-diagram of real SS of PZT system.](image-url)
Figure 2. Dependences of $V$, $\alpha$, $\Delta L/L$ on the temperature in the SS of the PZT system of various composition. The phases are indicated depending on the temperature [9, 10].
The analysis of the obtained dependences made it possible to distinguish three groups of SS with similar “behavior” of characteristics within each group. 

The first group includes SS with \( x < 0.04 \), which are characterized by pronounced anomalies of all characteristics (structural and thermophysical) inside the \( MR (R + Rh) \) at the Curie point, \( \Delta L/L \) is practically constant to the right of it, and \( \alpha \) is to the left and right of \( T_C \). \( V \) increases over the entire investigated range.

The second group is formed by a composition with \( 0.05 \leq x < 0.16 \) with a course \( \Delta L/L \) practically independent of temperature, a wavelike change in \( \alpha \), an invar effect of \( V \) near \( T_C \) and to the right of it, and weak growth at \( T > 650K \).

The third group consists of SS with \( 0.16 \leq x \leq 0.35 \) with a slight increase in \( \Delta L/L \) (up to 400K) and its subsequent sharp decrease in the range \( (400 \div 600) K \), ending at \( T \sim (600 \div 700) K \) with a slight rise in \( \Delta L/L \). The dependence \( \alpha(T) \) is extreme with a blurred minimum in the vicinity of \( T_C \). \( V \) increases nonmonotonically with increasing temperature.

This “behavior” of the analyzed parameters, in general, is typical for ferroelectric compounds and SS. The complex phase filling of objects, which determines the uniqueness of the thermodynamic prehistory of each SS, gives it some specificity.

Figure 3 shows the generalized data of \( \alpha, \Delta L/L \) obtained at different temperatures.

**Figure 3.** Dependences of \( \alpha, \Delta L/L \) on \( x \) at different temperatures in the \( \text{Pb (Zr}_{1-x}\text{Ti}_x\text{O}_3} \) system.
It is shown that as the temperature increases, $a$, $\Delta L/L$ at $x < 0.17$ experience non-monotonic behavior, with the formation of a number of extrema as Ti is enriched. A further increase in $x$ does not lead to significant changes and the dependences reach a plateau-like area. The data obtained correlate with the complex phase filling of the studied PZT system.

Thus, correlations between the thermophysical and structural parameters of the investigated solid solutions have been established. The obtained data are recommended to be used in the development of devices based on SS with the participation of the PZT system.

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