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## LETTER TO THE EDITOR

## The influence of the coexistence of ferroelectric and antiferroelectric states on the lead lanthanum zirconate titanate crystal structure

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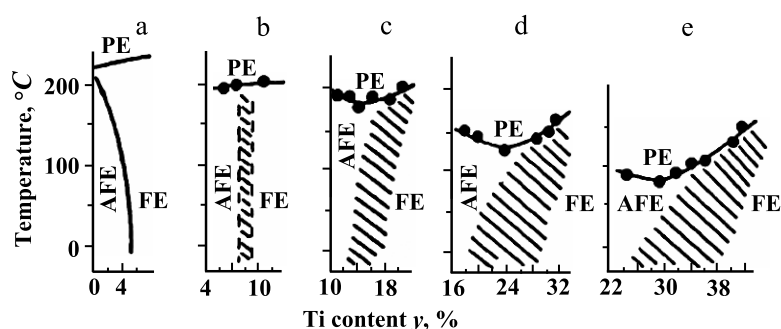
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Online at [stacks.iop.org/JPhysCM/17/L177](http://stacks.iop.org/JPhysCM/17/L177)**Abstract**

We present results of detailed investigation of the crystal structure of  $\text{Pb}_{1-3x/2}\text{La}_x(\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$  solid solutions. In this letter our attention is concentrated on the series of solid solutions with  $x = 6\%$  usually referred to as relaxor ferroelectrics. We have established the reasons for the non-cubic crystal structure of these solid solutions at the temperatures below  $T_C$ . It is demonstrated that the peculiarities of the properties of  $\text{Pb}_{1-3x/2}\text{La}_x(\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$  depend on the position of a particular solid solution with respect to the hysteresis ferroelectric–antiferroelectric region in the ‘Ti-content–temperature’ phase diagram.

Lead lanthanum zirconate titanate  $\text{Pb}_{1-3x/2}\text{La}_x(\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$  (PLZT) solid solutions were obtained from parent lead zirconate titanate  $\text{PbZr}_{1-y}\text{Ti}_y\text{O}_3$  compounds by substitution of La for Pb more than 30 years ago [1, 2]. PLZT compounds with particular compositions manifest a rather large value of piezoelectric effect. This circumstance makes them important for actuator applications. Other compositions possess a pronounced electro-optic effect and they are used for application in electro-optics. PLZT is also important for researchers engaged in investigations of fundamental properties of solids due to a variety of phase transitions possible in these substances. In particular, PLZTs with  $x \geq 6\%$  have been of significant interest in connection with investigations of the nature of the so-called relaxor ferroelectric (FE) state. There is no consensus on mechanisms determining the nature of the relaxor state at present. This is why intensive studies of substances that manifest the relaxor FE state are carried out to elucidate the peculiarities of their crystal structure [3–10].

The crystal structure of PLZT at room temperature was considered a pseudocubic perovskite during the first decade of studies. The type of distortions has not been identified



**Figure 1.** ‘Ti-composition–temperature’ phase diagrams for  $\text{Pb}_{1-3x/2}\text{La}_x(\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$  solid solutions with different La contents: (a)  $x = 0\%$ ; (b)  $x = 2\%$ ; (c)  $x = 4\%$ ; (d)  $x = 6\%$ ; (e)  $x = 8\%$ .

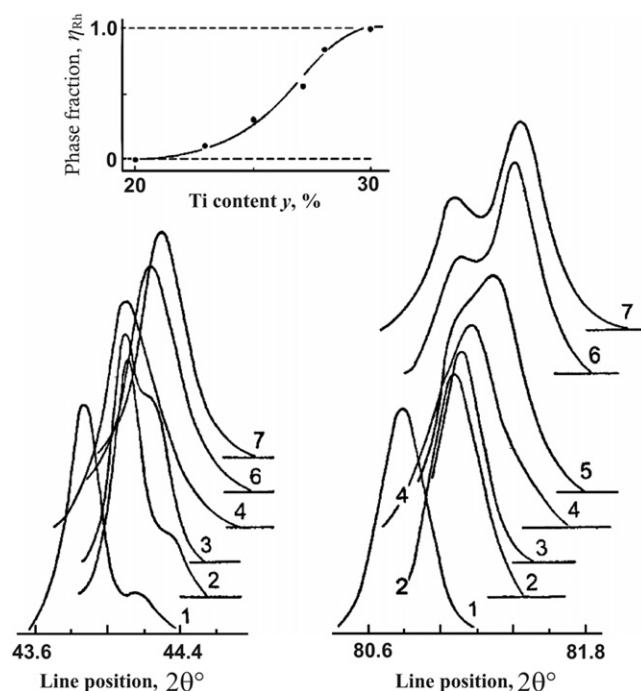
precisely; however, the term ‘pseudocubic’ has been used to show that the structure is non-cubic. Such a point of view was confirmed by a number of experiments [11–14]. Later, the crystal structure of solid solutions that manifest relaxor behaviour came to be considered as cubic, because it has been much easier to build simplified models of the FE relaxor state in such an approximation. Thus, the problem of determination of the PLZT crystal structure at the temperatures below the Curie point is topical at present.

The purpose of the present paper is to show that the crystal structure of PLZT solid solutions at temperatures below the Curie temperature is in fact non-cubic as well as to depict the factors which lead to difficulties in the structure identification.

A particular series of solid solutions was chosen for our experiments. It comprises solid solutions for which the room-temperature state is known beforehand to be either FE or antiferroelectric (AFE). The chosen series also contains the solid solutions that manifest the properties that cause intensive discussions in the literature. Investigation of the entire series of PLZT solid solutions with  $x = 6\%$  makes it easy to reveal the stage at which the solid solutions with FE ordering are changed by the ones with AFE ordering.

Samples of  $\text{Pb}_{1-3x/2}\text{La}_x(\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$  were obtained by the co-precipitation of components from the mixture of the aqueous solutions of lead and lanthanum nitrates and zirconium and titanium chlorides. After washing and drying the precipitates were calcined at 550 and 850 °C. Ceramic samples [15] were sintered at the temperatures 1320–1340 °C in a controlled PbO atmosphere. The grain size was from 5 to 7  $\mu\text{m}$ . X-ray diffraction confirmed that the samples were single phase with perovskite crystal structure. Structural analysis was performed with a Siemens D-500 powder x-ray diffractometer using a Ge monochromator ( $\text{Cu K}\alpha_1$  radiation of 1.54056 Å wavelength) on primary beam and a Braun gas position sensitive detector. The measurement conditions provided 0.01° resolution with respect to the angle  $2\theta$ . The x-ray diffraction measurements were realized at room temperature (20 °C). The samples were annealed at 600 °C for 4 h prior to the measurements and after annealing they were aged at room temperature for 6 months.

The evolution of the Ti-content–temperature phase diagram ( $Y$ – $T$  phase diagram) in the process of successive increase of the percentage of La substitution is presented in figure 1 (the construction of these diagrams is described elsewhere [16–18]). The boundary region (shown by dashes in figure 1) that separates the regions of FE and AFE ordering is shifted toward higher concentrations of Ti in the solid solutions with increase of the La content. This boundary region is the hysteresis region for the FE–AFE transformation. X-ray and transition electron microscopy studies of PLZT with compositions from this boundary region of the

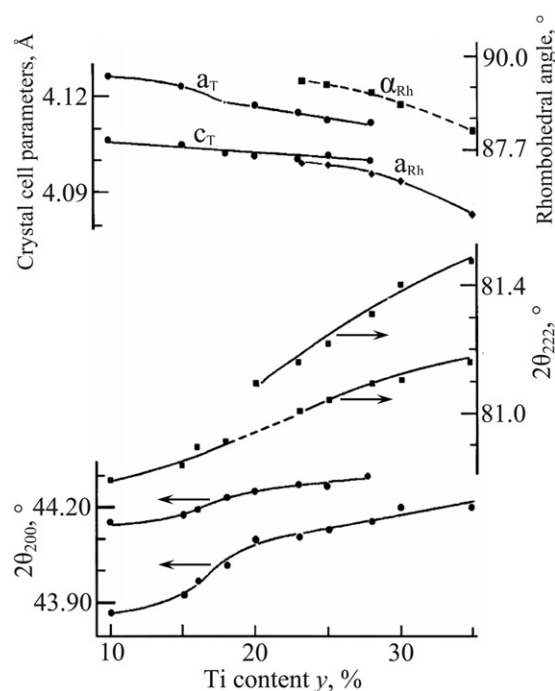


**Figure 2.** Profiles of the (200) (at the left) and (222) (at the right) x-ray lines for the series of solid solutions with 6% of La. The Zr and Ti content of solid solutions  $(100 - Y)/Y$ , where  $Y$  is the percentage of Ti: 1—90/10; 2—85/15; 3—80/20; 4—77/23; 5—73/27; 6—70/30; 7—65/35. The dependence of the fraction of rhombohedral phase in the sample volume on the content of Ti in solid solution is presented in the inset.

phase diagram [19, 20] have shown that the domains of FE and AFE phases coexist in the sample volume (the transition electron microscopy images of coexisting domains of FE and AFE phases one can find in [20]).

As seen in figure 1, the phase  $Y-T$  diagrams for all the series with the La content higher than 4% are equivalent from the viewpoint of physics. Therefore, the largest part of our study in the scope of the present work was carried out on PLZT with 6% of lanthanum.

We investigated the profiles of the x-ray diffraction lines in the solid solutions in question. Our attention has been focused on (200) and (222) x-ray diffraction lines, which are the most characteristic lines for studying the crystalline structure of perovskite type. The (200) line is a doublet in the presence of tetragonal distortions of the elementary cell, whereas the (222) line is a singlet in this case. In the presence of rhombohedral distortions the (200) line is a singlet and the (222) line is a doublet. These lines are shown in figure 2. The variation of profiles of these lines with the change of Ti content in solid solutions is clearly seen in figure 2. The complex character of profiles of x-ray lines undoubtedly proves that the crystal structure is not cubic at temperatures below the Curie point. The crystal structure in the AFE state is characterized by tetragonal distortions of the elementary crystal cell, whereas the one in the FE state undergoes rhombohedral distortions. In the case of tetragonal distortions, the x-ray patterns contain weak superstructure reflexes that substantiate the AFE ordering in these solid solutions. The splitting of the x-ray lines decreases when the composition reaches the boundary region separating the FE and AFE states in the  $Y-T$  diagram. The shape of the x-ray lines is also dependent upon the location of the solid solution in the  $Y-T$  phase diagram. In



**Figure 3.** Dependences of the crystal cell parameters on Ti content in PLZT with 6% of La are shown at the top of the figure. The parameters  $a_T$  and  $c_T$  correspond to the tetragonal (AFE) phase and the crystal cell parameter  $a_{Rh}$  and the  $\alpha_{Rh}$  rhombohedral angle are for the rhombohedral (FE) phase. Dependences of the positions (the  $2\theta_{200}$  and  $2\theta_{222}$  angles) of the peaks of components for the (200) and (222) x-ray lines on Ti content in PLZT with 6% of La are presented at the bottom of the figure.

particular, the intensity of components of the composite lines redistributes as the substance reaches the boundary region. Analysis of intensities of components of the (200) and (222) lines allows us to obtain the dependence of the fraction of the rhombohedral (FE) phase in the sample volume as a function of Ti content. This dependence is given in the inset in figure 2.

The position of the peak of each component of the x-ray diffraction line depends on the Ti content in the solid solution. The dependences of these positions on Ti content for the (200) and (222) x-ray lines are presented in figure 3. The dependence of the crystal cell parameters  $a_T$  and  $c_T$  for the tetragonal (AFE) phase and crystal cell parameter  $a_{Rh}$  and rhombohedral angle  $\alpha_{Rh}$  for the rhombohedral (FE) phase on the Ti content is shown in the upper part of the figure 3 to highlight the change of the solid solution crystal structure with the variation of composition.

The crystal structure of the solid solutions that belong to the boundary region of the  $Y-T$  diagram is two phase; that is, the phases with tetragonal and rhombohedral distortions of the perovskite elementary cell coexist. The simultaneous finite non-zero splitting of both (200) and (222) x-ray lines (see figures 2 and 3) and the widening and asymmetry of the lines (in particular, for PLZT with  $x = 6\%$  and  $Zr/Ti = 75/25$  these lines are quasi-singlet) is evidence of the two-phase structure of the solid solution with this composition. Thus, the crystal structure of PLZT with 6% of La is unambiguously non-cubic at temperatures below the Curie point. These results also demonstrate that the identification of the structure of the PLZT with 6% of La and the Ti concentrations from the boundary region of the  $Y-T$  phase

diagram can be hindered by the following circumstance. The domains of the FE and AFE phases coexist in the samples with compositions that belong to the boundary region. So, one can easily make a mistake while identifying the structure of PLZT from the boundary region, if the examination the structure of the solid solutions from all the regions of the  $Y$ - $T$  diagram has not been done. It also has to be noted that the intensity of the superstructure x-ray lines decreases when the composition of PLZT approaches the boundary region moving from the region of zirconium-rich solid solutions.

The change of the character of the (200) and (222) x-ray lines that reflects a change of the crystalline structure is caused by the interaction between the coexisting FE and AFE phases [21–23]. The contribution of this interaction increases as the PLZT composition reaches the value that corresponds to equal free energies of the FE and AFE phases. At the same time, the deviations from properties of ordinary FE or AFE phases become more pronounced in solid solutions that belong to the interval of compositions where the free energies of the FE and AFE phases are close or equal. These deviations revealed themselves, for example, in measurements of dielectric or electro-optical hysteresis loops, in dispersion of the dielectric permittivity in the vicinity of the point of paraelectric phase transition, and in the smearing of this phase transition.

In the PLZT with 8% of La the observed picture is more complicated. The increase of lanthanum amount diminishes the energy barrier that separates the free energy minima corresponding to FE and AFE states. Therefore, the interaction between these phases manifests itself greatly. The boundary region in the  $Y$ - $T$  diagram becomes wider and the degree of crystal lattice distortions decreases, so the x-ray splitting is less pronounced. One more circumstance that is important has to be noted. The morphotropic phase boundary that is located at the point that corresponds approximately to the composition  $Zr/Ti = 53/47$  [15] in the  $Y$ - $T$  diagram of  $PbZr_{1-y}Ti_yO_3$  is displaced towards the solid solutions with higher percentages of Zr as the La concentration increases. At 8–9% of La, the morphotropic boundary is observed in the vicinity of the 65/35 Zr/Ti composition [11]. This composition corresponds to solid solutions, which are called ‘relaxor ferroelectrics’ and are the object of active discussions in the literature. The substance with this composition contains three phases, and it is manifested in the observed structure of the x-ray lines. Each of these lines is a superposition of the ones of FE rhombohedral, FE tetragonal and AFE tetragonal phases. As far as we know, such a fact has not been considered at the identification of the crystalline structure of PLZT and consequently, at the decomposition of x-ray diffraction lines into simple components. Here we would like to mention that the transmission electron microscopy investigations [19, 20, 24, 25] of PLZT show that the size of the domains of the co-existing FE and AFE phases is of the order of 20–30 nm.

Complexity of identification of the crystal structure of PLZT is furthermore complemented by the specifics of the hot pressing method used for preparation of samples for which the data of crystal lattice investigations are available in the literature. According to [26] the hot pressing prevents achievement of a high degree of homogeneity due to such factors as violation of stoichiometry resulting from hot pressing, ‘underannealing’ effects caused by low temperatures applied in the process of hot pressing, and the presence of residual mechanical stresses arising in hot pressing. Even in the case when the hot-pressed PLZT samples have a high optical quality, some nanometre scale regions containing chemical elements that have not reacted completely are present in the samples’ volume. In particular, this was confirmed in [27] by means of transmission electron microscopy. It was demonstrated in [28–30] that the hot-pressed PLZT samples of high optical quality also contain nanodomains with the composition close to that of pure  $PbZr_{1-y}Ti_yO_3$ .

The results presented here explicitly demonstrate that the crystal structure of series of PLZT with 6% of La is non-cubic at temperatures below the Curie temperature. One can

identify it undoubtedly only if the solid solutions from different regions of the  $Y-T$  phase diagram are investigated simultaneously. There is a considerable probability of error in the structure identification when only one solid solution belonging to the boundary region of the  $Y-T$  phase diagram (dashed regions in figure 1) is studied. It is also worth mentioning that the coexistence of FE and AFE phases or the even more complicated three-phase structure of PLZT with La content  $\geq 6\%$  could be the reason for relaxor behaviour at the phase transition from the paraelectric to the dipole ordered phase [31, 32].

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