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The kinetics of the local compositional changes at the ferroelectric–antiferroelectric interphase boundaries in lead–lanthanum titanate–zirconate solid solutions

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Abstract

The process of local decomposition of lead–lanthanum zirconate–titanate solid solution in the vicinity of the interphase boundaries separating domains of coexisting ferroelectric and antiferroelectric phases has been investigated. The kinetics of the local decomposition of the solid solution containing 6 at.% La, 73 at.% Zr, and 27 at.% Ti in the process of ageing of samples quenched down to room temperature from the paraelectric phase is studied. The mechanisms that define the kinetics of the process of attainment of the equilibrium state of coexisting domains of ferroelectric and antiferroelectric phases are analysed. It is demonstrated that there are two main mechanisms determining the kinetics of establishing of the equilibrium inhomogeneous chemical composition of a solid solution. The slower mechanism is determined by the diffusion of the oxygen vacancies, the nonequilibrium concentration of which was created during the annealing at the temperatures above the Curie temperature. The faster process is determined by the cation diffusion caused by the local mechanical stresses in the vicinity of the interphase boundaries. The equilibrium structure establishes during a time interval of not less than 120 h.

1. Introduction

Compounds with an inhomogeneous state of coexisting phases have attracted a great deal of interest because of the fundamental problems of multiphase system stability and the nature of the phase transitions between phases. Compounds with inhomogeneous states of coexisting phases are widely known among magnetic and superconducting materials and are important for technological applications. Such magnetic materials are the hard magnetic materials that can

store high amounts of magnetic energy [1, 2]. The type II superconductors comprise another group of materials with inhomogeneous phase states. From the viewpoint of microstructure, type II superconductors are inhomogeneous structures in which an external magnetic field leads to the coexistence of the superconducting and normal phases [3]. This coexistence of normal and superconducting phases provides high values of the critical current.

The solid solution inorganic ferroelectric materials are not only multiphase systems, but exhibit very large piezoelectric coefficients, making such materials attractive for a number of applications. During the past 10–15 years, considerable attention has been paid to ferroelectric compounds with inhomogeneous structures: lead zirconate–titanate (PZT: $\text{PbZrO}_3\text{--PbTiO}_3$) based solid solutions, lead magnesium niobate–lead titanate (PMN–PT: $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--PbTiO}_3$), and lead zinc niobate–lead titanate (PZN–PT: $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--PbTiO}_3$) [4–6]. In all these compounds, high values of piezoelectric parameters have been observed in precisely those solid solutions which exist in the so-called morphotropic region on the phase states diagram. This morphotropic region of the phase diagram is characterized by the coexistence of domains of ferroelectric phases with tetragonal and rhombohedral types of crystal cell distortions [7–11].

The lead–lanthanum zirconate–titanate solid solutions (PLZT: $(\text{Pb}, \text{La})(\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$) are one more example of a system with coexisting phases. The high values of electro-optic characteristics are unique to solid solutions that possess domains of coexisting ferroelectric and antiferroelectric phases [12, 13].

An interphase domain wall separates the domains of the ferroelectric and antiferroelectric phases, and the said phases have different sizes of elementary crystal cell. It has been shown by the method of transmission electron microscopy [14, 15] that no dislocations are observed at these interphase boundaries. This indicates that across the interphase domain wall, from one phase to the other, there are no breaks of crystal planes. Such a nearly continuous interphase domain wall structure leads to an increase of the elastic energy. The greater is the difference in the configuration volumes of the coexisting ferroelectric and antiferroelectric phases the greater is the increase in elastic energy. The local strain defines the positive value of the interfacial energy density at the boundaries separating ordinary domains in ferroelectrics [13, 16].

In the substances considered in this paper the equivalent crystallographic sites are occupied by ions differing either in size or in charge or in both. In a single-phase state (inside the domains of each of the coexisting phases), each of the ions, forming the crystal lattice, is not subjected to a net force (more correctly, the resultant force affecting each ion is equal to zero) in the absence of external factors. The balance of forces affecting each of the ions located near the ‘bare’ interphase domain wall is upset. ‘Large’ ions are pushed out into those domains, which have a larger configuration volume and, consequently, a larger distance between crystal planes. ‘Small’ ions are pushed out into the domains with a smaller configuration volume and smaller interplanar distances of the crystal lattice. Such a process is accompanied with both a decrease of the elastic energy concentrated along the ‘bare’ interphase domain wall and an increase of the energy associated with the local decomposition of the solid solutions in the vicinity of the said wall. The processes of local decomposition and ion segregation will be completed when the newly formed interphase domain wall structure provides the energy minimum.

Local decomposition in the vicinity of the ferroelectric–antiferroelectric interphase domain boundary was first observed in $(\text{Pb}, \text{Li}_{1/2}\text{La}_{1/2})(\text{Zr}_{1-y}, \text{Ti}_y)\text{O}_3$ solid solutions (PLLZT) [17–19]. However, the kinetics of the local decomposition of the solid solution has not been investigated up to now.

The main goal of the present paper is the investigation of the kinetics of local decomposition of PZT based solid solution, for which domains of ferroelectric and antiferroelectric phases coexist. The detailed investigation was performed on lead–lanthanum

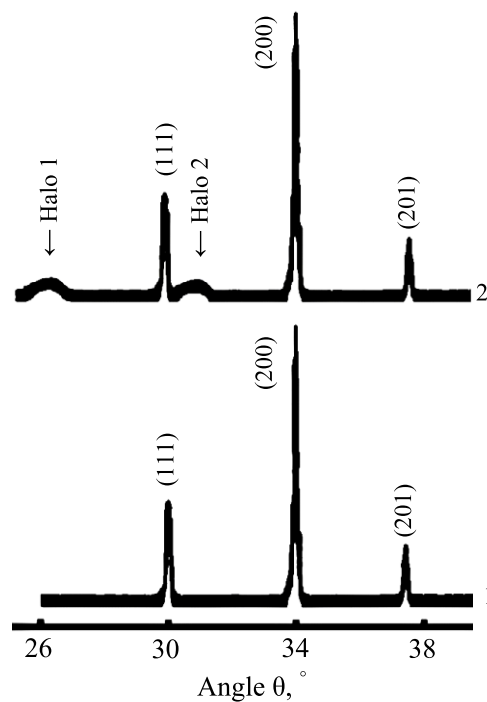


Figure 1. X-ray diffraction patterns of 6/73/27 PLZT solid solution obtained at the room temperature right after the quenching (1) and after ageing during 30 days (2).

zirconate–titanate solid solution with the following composition: 6 at.% La, 73 at.% Zr, and 27 at.% Ti. In what follows, we will use the standard denotation: 6/73/27 PLZT. As was shown before [12, 20, 21], domains with ferroelectric and antiferroelectric types of ordering coexist in this solid solution. The presence of this coexistence of phases was proved by means of the x-ray diffraction method, and transmission electron microscopy, as well as what follows from the analysis of the evolution of phase diagrams in the process of substitution of lanthanum for lead in PZT solid solutions.

2. Experimental methods

Ceramic PLZT samples were obtained by the method of joint co-precipitation from the mixture of aqueous solutions of lead and lanthanum nitrates and chlorides of titanium and zirconium with subsequent two-stage synthesis at 550 and 850 °C. The polycrystalline samples were obtained by sintering at 1300–1340 °C in a controlled PbO atmosphere. The resulting grain size was found to be 6–8 μm . X-ray diffraction analysis confirmed that the samples were single phase with perovskite crystal structure.

The decomposition of the solid solution is manifested in the appearance of weak diffusion lines (halos 1 and 2 in figure 1, pattern 2) in the x-ray diffraction patterns near the basic diffraction lines characteristic of the perovskite structure of the solid solutions investigated [18, 19]. While investigating the dynamics of the formation of segregates in the process of local decomposition of a solid solution it is necessary to measure x-ray patterns during a short period of time in a wide interval of x-ray beam scattering angles. Due to a low

intensity of diffuse lines, the process of measurement at each point must be long enough for the measurement to be both representative and valid.

In connection with the discussion above, the mesoscopic structure of the solid solution (segregation structure) was investigated by the Debye–Scherrer method (on the sample's metallographic section) with subsequent photometry of the x-ray patterns. This method makes it possible to take measurements synchronously in a wide interval of angles, which is very important for investigation of the kinetics of the process. Co $K\alpha$ radiation filtered by a layer of vanadium oxide was used. The angular speed of a flat sample was 1 rpm. The duration of the survey was 20 min (10 min for each position of the sample plane, symmetric with respect to the incident x-ray beam).

3. Results

As a first step, a sample of the 6/73/27 PLZT solid solution was annealed at 600 °C for 22 h. The x-ray patterns that were obtained at 600 °C on the annealed samples contained only strong singlet x-ray lines caused by the coherent scattering from crystal planes of perovskite cubic lattice. Please note that the ferroelectric Curie temperature of the PLZT solid solution under investigation is $T_C \approx 160$ °C, well below the annealing temperature, but well above the ageing temperature.

After the high-temperature x-ray studies the samples were quenched to room temperature and then left to age at 22 °C during the time interval τ . At the end of each time interval τ the x-ray studies of local decomposition structure were carried out by the Debye–Scherrer method. Right after quenching ($\tau \approx 0$) the x-ray patterns contained only strong singlet diffraction lines as in high-temperature case (figure 1, pattern 1). The structure of the x-ray patterns becomes more complicated during ageing. A splitting of the singlet lines takes place. Broadened diffuse lines (halos) with a significantly lower scattering intensity appear in addition to the diffraction lines (figure 1, pattern 2). These new lines are caused by the incoherent scattering from chaotically oriented segregates at the interphase ferroelectric–antiferroelectric boundaries [18, 19]. We studied the behaviour of the halos in the two intervals of angle $\theta = 25^\circ\text{--}27^\circ$ (Halo 1) and $\theta = 29^\circ\text{--}32^\circ$ (Halo 2). The intensity, location, and shape of the halo change with time. The shape and location of the diffraction lines, which characterize the crystal structure of the solid solution under investigation, also change with time.

The dependence of the elementary cell volume (the calculations were made based on the position of the (200) x-ray diffraction peak in the pseudo-cubic approximation) on the ageing time for the PLZT solid solution under investigation is shown in figure 2. In the first stage of the process of ageing (of about 15–20 h), the volume of the elementary cell of the perovskite crystalline structure of the solid solution increases. At longer ageing times, the volume decreases. As one can see, the change of the volume that occurs virtually follows an exponential behaviour for both the first and the second stage of ageing.

The shape, intensity and position of the halos as functions of ageing time are presented in figures 3 and 4. The following peculiarities of these dependences attract attention. During the ageing process, both the variation of the profile and the angular position of the diffuse scattering lines changes. It should be mentioned that there is a clear correlation between the change of the positions of the x-ray diffraction lines (figure 5) and the change of the location of the diffuse scattering lines. The dependence of the intensity of the diffuse lines on the ageing time reaches saturation in approximately 25 h.

Changes in the shape and position of x-ray diffraction lines during the samples' ageing process are given in figure 6. We analysed the behaviour of the (111) and (200) lines which are the most typical for the perovskite structure of the solid solutions investigated. The former line is a singlet in the case of tetragonal lattice distortions, and it is a doublet in the case of

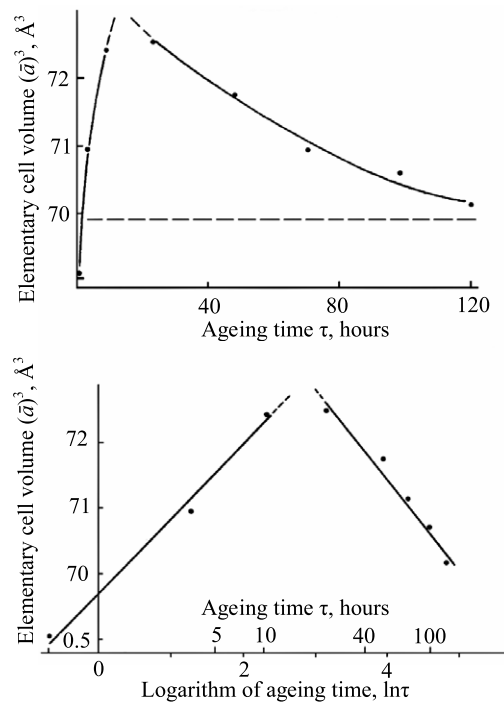


Figure 2. Dependence of the elementary cell volume on the ageing time for the 6/73/27 PLZT solid solution.

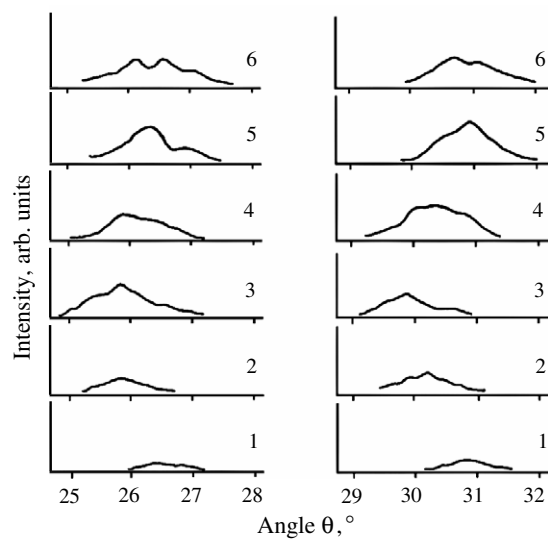


Figure 3. Changes of profile and position of the halos in the process of ageing after the quenching of the 6/73/27 PLZT solid solution. Ageing time (hours): 1—0.5, 2—3.5, 3—23, 4—48, 5—72, 6—120.

rhombohedral distortions. On the contrary, the latter line is a doublet in the first case and a singlet in the second case.

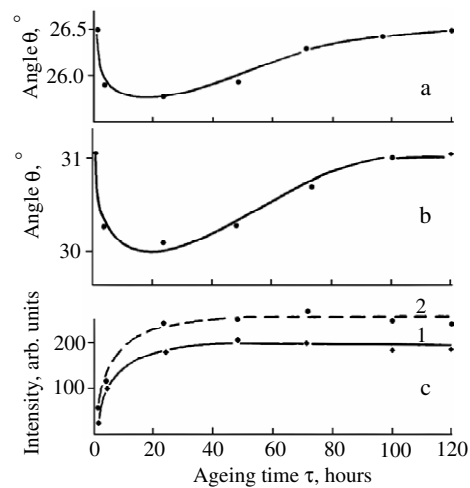


Figure 4. Ageing time dependences of positions of two diffuse lines: halo 1 (a), and halo 2 (b). Dependences of the intensity of the two diffuse lines on the ageing time (c): 1—halo 1, and 2—halo 2.

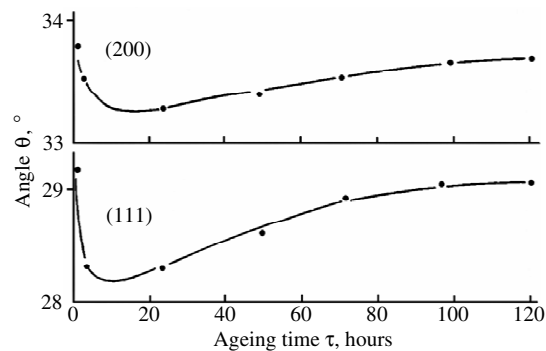


Figure 5. The dependence of positions of the (111) and (200) x-ray diffraction lines on ageing time for the 6/73/27 PLZT solid solution.

Analysis of the profile of the said diffraction lines allows us to infer a structural relationship between the low-temperature phases during the process of ageing. Immediately after quenching, the phase with the tetragonal type of the perovskite crystal structure distortions predominates in the bulk of the sample. Then the phase with the rhombohedral type of distortions grows to dominate, with some ageing. Only with further ageing the low-temperature phases, namely, the phase with the tetragonal type of lattice distortions and the phase with the rhombohedral type of lattice distortions coexisting as the equilibrium two-phase structure are established in the bulk of the sample.

4. Discussion

The Ti-content versus temperature phase diagram of PLZT solid solutions with 6 at.% content of lanthanum [12, 21] is shown in figure 7 (at the bottom). The dependence of the fraction of

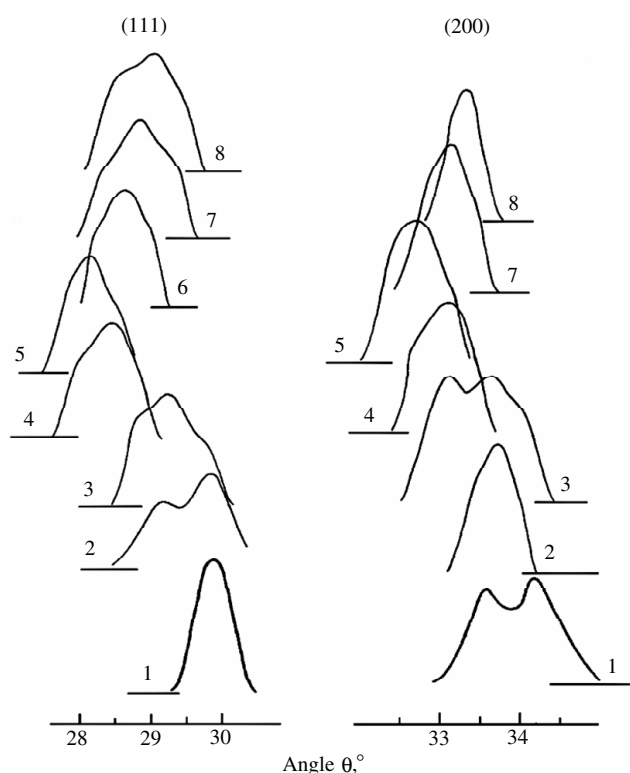


Figure 6. Variations in the shape and position of the (111) and (200) x-ray diffraction lines in the process of the samples' ageing after quenching of the 6/73/27 PLZT solid solution. Ageing time (hours): 1—0.25, 2—0.5, 3—3.5, 4—23, 5—48, 6—72, 7—96, 8—120.

rhombohedral phase in the sample volume on the Ti-content in this system of solid solutions is shown in the upper part of this figure. As one can see from figure 7, the phase state of the 6/73/27 solid solution is two-phase at low ($T < T_C$) temperatures. The domains of ferroelectric and antiferroelectric phases coexist in the sample volume. It is known that the characteristic time of establishment of the equilibrium low-temperature state at the structural phase transitions is of the order of 10^{-4} – 10^{-6} s [22]. The paraelectric–ferroelectric or paraelectric–antiferroelectric phase transitions are also structural ones. Therefore, all the processes that we investigated in this study take place in a system which is essentially a two-phase system containing domains of ferroelectric (FE) and antiferroelectric (AFE) phases. Thus, one has to take into account the two-phase nature of the system and the presence of the interphase boundaries while interpreting the results.

The time dependences of the shape and the intensity of diffuse x-ray lines (halos), as well as the absence of the said lines in the x-ray patterns obtained at 600 °C, confirms the connection between the long-term relaxation and the formation of segregates in the vicinity of the interphase ferroelectric to antiferroelectric phase boundaries. The establishment of an equilibrium state is a long-term process in solid solutions in which the state of coexisting ferroelectric and antiferroelectric phases is realized. As one can see from the x-ray data, it continues for not less than 120 h. However, taking into account the limited sensitivity of this method one can assert that this process takes even longer.

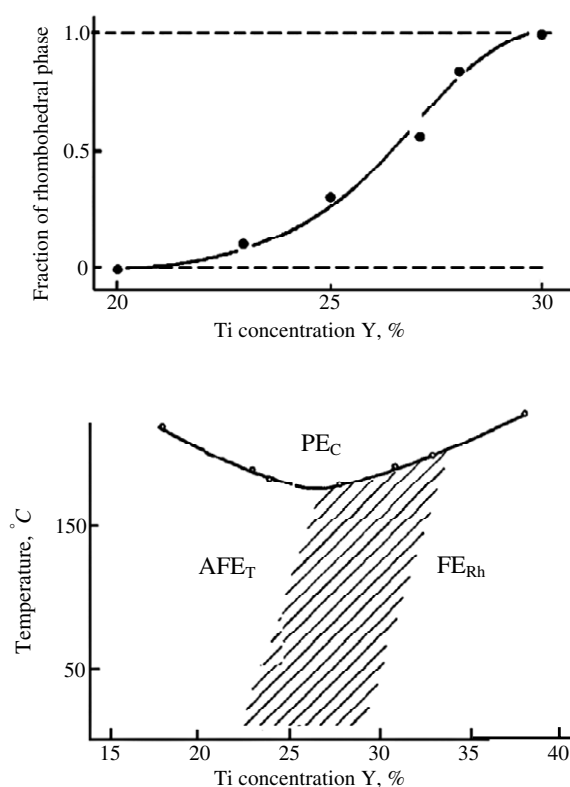


Figure 7. Top: the dependence of the fraction of the rhombohedral phase in the sample volume on the concentration of Ti in the PLZT series of solid solutions with 6% La. Bottom: Ti-content versus temperature phase diagram for the same series of solid solutions. The region shown by dashes is the interval of the solid solution compositions characterized by the coexistence of the domains of the FE and AFE phases in the bulk of the sample.

The segregation processes are multistage. It is clearly seen from the results given in figures 2–6 that there are different relaxation times caused by different mechanisms. In addition to segregation, one has to note that the mechanisms responsible for establishment of equilibrium values of the structural order parameters occur on the timescale of $10\text{--}10^{-4}$ s (such time intervals are beyond the abilities of our experimental methods). Without elucidation of particular mechanisms responsible for attainment of the equilibrium state, one can assume that the long time constant of this process is connected with the diffusion processes associated with the local decomposition of the solid solutions along the interphase domain boundaries. The estimation of the size of the segregates (using the shape of the diffused x-ray lines) gives values of 8–15 nm [17, 18] (a similar approach to estimations of the average size of nanoregions one can be found in [23–25]).

Long-term relaxation processes are non-monotonic processes due to the condition of ‘strong deviation from equilibrium’ in the initial stages following quenching. In the case of ‘weak deviation from equilibrium’ (at the final stage) the relaxation process is monotonic and is described by an exponential law. Nonetheless, the PLZT and PLLZT solid solutions do differ by the presence of vacancies in the A-positions of the crystal lattice of the PLZT system of solid solutions. There is a peculiarity of the ageing process for the PLLZT system of solid

solutions occurring at ageing times 20–30 h, which were attributed to accumulation of elastic stress and the subsequent drop in strain [19], not present in the PLZT system. Otherwise, the compositional (and structural) relaxation process follows similar patterns for both the PLZT and PLLZT solid solutions systems.

Now let us dwell on the mechanisms defining the kinetics of the processes in question at different time periods (stages). There are different mechanisms, which contribute to the long-term relaxation. Two mechanisms should be pointed out among the many mechanisms. The contribution of the crystal lattice defects, in particular oxygen vacancies and the diffusion of the cations in the vicinity of the interphase boundaries, caused by local mechanical stresses, command the greatest attention. Under the conditions of our experiments the concentration of the vacancies in the lead sites remained practically constant because the volatilization of lead in the PLZT solid solutions starts only at temperatures $T > 800^\circ\text{C}$. The difference in size (and, consequently, in mobility) and charge of the ions, which are located in the equivalent sites of the crystal lattice, should be taken into account. At the same time a permanent rearrangement of the multiphase domain structure also takes place. This domain structure rearrangement is due to the change of the local composition of the solid solution and, as a consequence, to the change of the local phase stability. Complete analysis is still beyond our grasp as the influence of the oxygen sublattice defects on the crystalline structure of these solid solutions is insufficiently characterized at present, but by drawing from the experimental results obtained for related oxide materials with perovskite or perovskite-type structures, some additional insights are possible.

Annealing of the samples at 600°C leads to the growth of the concentration of oxygen vacancies; the equilibrium concentration of the oxygen vacancies grows rapidly as the temperature rises. Quenching down to room temperature leads to freezing of the non-equilibrium elevated concentration of the vacancies in the bulk. Oxygen vacancies in ionic-covalent compositions, to which the solid solutions with perovskite structure belong, lead to an increase of the crystal lattice parameters [26–28]. Alongside the increase in lattice parameter, vacancies in perovskite and perovskite-like compositions favour the increase of the stability of the phases with tetragonal type of crystal lattice distortions.

During the ageing process the oxygen vacancies move towards the sample surface and leave the sample (actually, the diffusion of oxygen into the bulk of the sample across the surface takes place) and, as a consequence, the crystal lattice parameters decrease. Since at room temperature the diffusion coefficient is comparatively low, and the surface maintains a steady state concentration of vacancies, the said process is the long-term one.

Let us consider the ion diffusion in the vicinity of the domain boundaries separating domains of the ferroelectric and antiferroelectric phases. Mechanical stresses arise at these interphase boundaries after the quenching and formation of domains of the coexisting ferroelectric and antiferroelectric phases inside the sample's volume. These stresses are caused by the difference of the interplanar distances in the neighbouring domains. There is an associated increase in the elastic energy. This increase in strain is reduced by the redistribution of the ions in the vicinity of the interphase boundaries and, as a result, by the local decomposition of the solid solution and the formation of segregates. Since mechanical stresses are now the motive force of ion diffusion, this process must have a higher rate than the process of establishment of the equilibrium concentration of the oxygen vacancies. As is seen from figure 4(c), the dependence of the intensity of the diffuse x-ray lines, connected with the formation of the segregates, on the ageing time reaches saturation already in 20–25 h.

Ions that essentially differ in ionic radii (and charge) participate strongly in the diffusion processes, which define the formation of the segregates and the local decomposition. These are lead ions Pb^{2+} and lanthanum ions La^{3+} which occupy the A-sites of perovskite crystal lattice, and zirconium Zr^{4+} and titanium ions Ti^{4+} , which occupy the B-sites of the crystal lattice.

Obviously, the rates of their diffusion differ as well. This leads to the change of the chemical composition both of the segregates and the solid solutions inside the domains with time. As the ions with smaller ionic radii from the domains of one of the coexisting phases reach the interphase boundary, the solid solution inside the domains becomes enriched with ‘larger’ ions. As a consequence, the position of the solid solution in the phase Y–T diagram changes in time, the crystal lattice parameters increase and the type of the crystal lattice distortion changes. This is clearly seen in figure 6. When at the first stage of the local decomposition ‘small’ lanthanum and titanium ions reach the interphase boundaries, the composition of the solid solution inside the domains correspond to PZT with an elevated content of zirconium. Such solid solutions are characterized by the rhombohedral type of crystal lattice distortion. Therefore, as the intensity of the diffuse lines grows, the profile of the x-ray diffraction lines changes, which points to the fact that the predominating amount of the tetragonal phase is replaced by that of the rhombohedral phase. That is, the share of the rhombohedrally distorted phase in the bulk of the sample increases.

At this stage of the process the change of the elementary cell volume is defined by the competition of two processes—the reduction of the volume owing to the decrease of the concentration of the oxygen vacancies and the increase of this volume due to the enrichment of the composition inside the domains with the ‘larger’ ions. The diffusion of oxygen vacancies is the slower process. As a result, in the first stage of ageing the volume increases and a maximum value is achieved in approximately 20 h.

As further ageing takes place, the ‘larger’ zirconium and lead ions reach the interphase boundaries and the composition inside the domains approaches its nominal formula composition; the solid solution regains its stable location on the composition versus temperature phase diagram (that is, a return to the two-phase region of the state diagram takes place). In the profiles of the x-ray lines this fact manifests itself (after approximately 50–60 h of ageing) by gradual establishment of precisely such shape that is characteristic of the domains after sintering and ageing on a very long timescale (the line shape that is established after one year).

The changes in the diffusive scattering profile also take place during the above-described ageing process. These changes confirm the fact that the concentration of different ions in the segregates varies at the interphase boundaries. The profile of the diffusive lines is defined by the resulting enveloping curve obtained after summation of the x-ray scattering from the crystal planes in the segregates. Since the local chemical composition of the segregates constantly changes in the process of ageing after quenching, the profile of the diffusive lines changes as well.

The results reported in a previous paper [20] show that it is difficult enough to identify the crystalline structure of PLZT solid solutions with 6 at.% La, at temperatures lower than that of the maximum of the $\varepsilon(T)$ dependence in the transient region of the composition versus temperature phase diagram. This is connected with the fact that the domains of the FE and AFE phases coexist in the bulk of the samples of those PLZT solid solutions, which belong to the shaded region in figure 7, and the effects caused by the interaction of these domains [29–31] manifest themselves. The coexistence of the ferroelectric and antiferroelectric phases also leads to certain peculiarities in the physical properties of those solid solutions, which are located in the said region of the phase diagram. These peculiarities distinguish the substances with coexisting ferroelectric and antiferroelectric phases from ordinary ferroelectrics or antiferroelectrics. These peculiarities are manifested, for example, in the dielectric or electro-optical hysteresis loops, in the dispersion of the dielectric permittivity in the vicinity of the paraelectric phase transition, and in the diffuse nature of this phase transition [12].

As we have indicated, there are many difficulties in the identification of the crystal structure that are connected with the local decomposition of the solid solutions in the vicinity of the

boundaries between the coexisting phases. The formation of the mesoscopic structure of segregates at these boundaries in the bulk of the samples poses a particular problem. In the x-ray diffraction patterns it manifests itself in the appearance of supplementary diffuse lines that accompany the diffraction lines, on which basis the PLZT crystal structure is actually identified. Often these diffuse lines may appear as satellites of the main Bragg peaks. In this case, in the process of mathematical treatment of the experimental x-ray diffraction patterns according to the existing programs a third phase is brought into consideration. We have faced such a phenomenon while treating the experimental results. This is connected only with the fact that in the development of the corresponding programs the phenomenon of local decomposition of the solid solution has not been taken into account. As far as we know, the effects associated with the coexistence of ferroelectric and antiferroelectric phase domains and the local decomposition of the solid solution in the vicinity of the interphase boundaries have not been discussed in the literature up to now.

In general, the structural analysis is more difficult with the increase of La-content. The increase of La-content diminishes the energy barrier that separates the free energy minima corresponding to ferroelectric and antiferroelectric states. Therefore, the interaction between these phases manifests itself greatly. The boundary region in the 'Ti-content-temperature' diagram becomes wider, and the degree of crystal lattice distortion decreases, so the x-ray splitting is less pronounced. One more important circumstance is noteworthy. The morphotropic phase boundary located at the point approximately corresponding to the composition $Zr/Ti = 53/47$ [32] in the 'Ti-content-temperature' diagram of $PbZr_{1-y}Ti_yO_3$ is now shifted towards solid solutions with higher concentrations of Zr as the La concentration increases. In the PLZT with 8 at.% La the situation is quite complicated. At 8–9% La, the morphotropic boundary is observed in the vicinity of the 65/35 Zr/Ti composition [33]. This composition corresponds to the solid solutions called 'relaxor ferroelectrics'. Materials with such a composition contain three phases, and their presence is evident from the observed complex structure of the x-ray diffraction lines. Each of the pertinent x-ray lines is a superposition of the expected lines for FE rhombohedral, FE tetragonal and AFE tetragonal phases. As far as we know, such a fact has not been considered in the identification of the crystalline structure of PLZT and, consequently, in the decomposition of x-ray diffraction lines into simple components. Here we would like to mention that transmission electron microscopy investigations [34–36] of PLZT show that the size of the domains of the coexisting FE and AFE phases is of the order of 20–30 nm. As a consequence an additional broadening of the x-ray diffraction lines is possible.

The identification of the PLZT crystal structure is affected by the sample preparation method. Such is the case for the hot pressing method used for the preparation of some samples. According to [37], hot pressing prevents the attainment 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 with 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 in the process of PLZT fabrication, are present in the samples' volume. In particular, this fact was confirmed in [38] by means of transmission electron microscopy. As demonstrated in [39–41], hot-pressed PLZT samples of high optical quality also contain nanodomains with a composition close to that of pure $PbZr_{1-y}Ti_yO_3$.

The results presented here and in [20] explicitly demonstrate that the crystal structure of the PLZT series with 6% La at temperatures below the Curie temperature is complicated. One can identify it with certainty only if solid solutions from different regions of the composition versus temperature 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 composition versus temperature phase diagram (dashed region in figure 6) is studied. It is also worth mentioning that the coexistence of ferroelectric and antiferroelectric phases or the even more complicated three-phase structure of PLZT with La-content >6% could be the reason for extraordinary behaviour at the phase transition from the paraelectric to the dipole-ordered phase [42, 43].

5. Conclusion

Investigation of formation of mesoscopic structures in the process of spontaneous transition from a single-phase paraelectric state to a two-phase state of coexisting domains of the ferroelectric and antiferroelectric phases in the solid solutions that allow the coexistence of the ferroelectric and antiferroelectric phases at the temperatures below the Curie point has been carried out. The PLZT solid solution is considered as an example. It is demonstrated that the formation of mesoscopic structures is accompanied by the local decomposition of the solid solution in the vicinity of the interphase boundaries. This process is also followed by the emergence of the chemical inhomogeneity of the substance. The said process is realized by means of ion diffusion at relatively low temperatures ($T < T_c$) when the diffusion coefficients are small, and thus the process is a long-time one at the room temperature: it continues for not less than 120 h. The process is a multistage one and the relaxation times at each stage are caused by different mechanisms. The size of the segregates estimated using the shape of the diffused x-ray lines has values of 8–15 nm.

Two main mechanisms defining the kinetics of the processes responsible for the formation of the solid solution's mesoscopic structure at different stages are emphasized among other mechanisms. The contribution of the oxygen vacancies (in our experiments the concentration of the vacancies in the lead sites remained practically constant) is the first mechanism and the second one is the diffusion of the cations in the vicinity of the interphase boundaries caused by local mechanical stresses. The permanent rearrangement of the multiphase domain structure takes place at the same time. This domain structure rearrangement is due to the change of the local composition of the solid solution and, as a consequence, to the change of the local phase stability.

The local decomposition of solid solutions in the vicinity of the boundaries between the coexisting phases and the formation of the mesoscopic structure of segregates at the said boundaries in the bulk of the samples create additional difficulties in the identification of the crystal structure of the PZT-based solid solutions as well as a number of other substances that allow the coexistence of phases. This phenomenon manifests itself in the x-ray patterns by the appearance of supplementary diffusive lines which accompany the x-ray diffraction lines, on which the base crystal structure of solid solutions is actually identified. These diffuse lines may often appear as satellites of the main x-ray diffraction lines. In this particular case a third phase is introduced into consideration in the process of mathematical treatment of the experimental x-ray diffraction patterns by means of existing methods and computer programs.

Acknowledgments

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