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Solid solutions with coexisting ferroelectric and antiferroelectric phases for creation of new materials

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The controlled decomposition of solid solutions in the vicinity of interphase boundaries separating domains of the coexisting antiferroelectric and ferroelectric phases opens new fields of applications for these materials. The lead zirconate–titanate based solid solutions are considered as an example of substances suitable for creation of materials with the negative refractive index. Manufactured composites constitute a dielectric antiferroelectric matrix with a structure of conducting interphase boundaries separating domains of the ferroelectric and antiferroelectric phases. The electric conductivity of the interphase boundaries occurs as a result of the local decomposition of the solid solutions in the vicinity of these boundaries. The decomposition process and consequently the conductivity of the interphase boundaries can be controlled by means of external influences.

Keywords: ferroelectric, antiferroelectric, phase coexistence, local decomposition, nanostructure, negative refractive index.

1. Introduction

Experimental confirmations of materials with negative refractive index predicted in Ref. 1 appeared in Refs. 2, 3. Researches worldwide manifest an increasing interest in such materials and the number of publications steadily increases. Comprehensive reviews [4–7] on properties and possible applications of negative refractive index materials have touched practically all aspects of this part of material science.

The first negative refractive index materials for only high frequency region of electromagnetic radiation spectrum were a composite construction of complex-shape elements [2,3,8] (for example, a periodic array of split-ring resonators with wires placed uniformly between the split rings and so on). It is impossible to use similar design for the optical range of spectrum. The materials for the near infrared and optical ranges of spectrum were the metal–dielectric composites [9–11]. Technological approach to manufacturing mentioned in Refs. 9–11 is quite laborious and is difficult to reproduce.

A feasible method for obtaining the dielectric–metal composite structures with the periodic arrangement of metallic inclusions is presented. Dimensions of these inclusions are from 8 to 12 nm, the periodicity of their arrangement can be varied from 0.2 to 2.0 µm. This method uses the local decomposition of the sold solution containing coexisting domains of the ferroelectric (FE) and antiferroelectric (AFE) phases. The decomposition of the sold solution takes place on the boundaries that separates the domains of FE and AFE phases [12–14]. Such boundaries (or segregates) possess the metallic type of conductivity.

Conductivity of the oxides with the perovskite crystal structure, for example, $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) can be changed by means of ion substitutions in lattice sites in a very wide range from pure dielectric state (with resistance of the order of 10^{14}–10^{16} Ω·cm) to the conducting state (with resistance of the order of 100 mΩ·cm).

The chemical composition of segregates precipitated along the interphase boundaries is slightly different from the maternal of the base solid solution [15]. Special selection of the chemical composition of the maternal solid solution along with the control of the chemical composition of segregates allow these segregates possess a diverse set of physical properties. The segregates manufactured by controlled local decomposition of solid solutions with proper chemical composition can be magnetic, dielectric or conducting.

In the present study we performed the decomposition of solid solution in such a way that the segregates in the vicinity of interphase boundaries had high (near-metallic) conductivity. PZT-based solid solutions are the most studied substances in which the FE and AFE ordering takes place. These materials are characterized by a small difference in free energies of the FE and AFE states in the solid solution with specific concentrations of components ($PbZrO_3$ and

$PbTiO_3$). At the same time, domains of the above-mentioned phases may coexist in the volume of solid solutions [15–18]. The metastable phase domains have the shape of cylindrical domains imbedded into the stable phase matrix in thin crystals [15,16] or the shape of ellipsoids of revolution close to spheres in the bulk crystals [19].

The relative stability of the FE and AFE phases depends on the relation between the concentrations of the solid solution components. The relative stability of phases and along with it the volume share of phases in the sample can be changed by varying the Zr–Ti-content of the solid solution. The sizes of the metastable phase domains and their density (the period of the domain structure) change when the share of this phase in the solid solution varies. The density and size of the domain structure can be also changed by means of the variation of an external electric field intensity as well as mechanical stress (pressure, uniaxial or biaxial compressions or tensile stress), since these external influences affect the relative stability of the FE and AFE phases. Under the lateral strains the cylindrical domain structure is transformed into the stripe-domain one.

Let us briefly describe the decomposition process in solid solutions in the vicinity of the interphase boundaries. These boundaries separating the adjacent FE and AFE domains are characterized by the continuous conjugation of crystal planes [15,16,20] (without discontinuities of crystal planes and dislocations at the interphase boundaries). Such coherent character must be accompanied by an increase in the elastic energy of the crystal lattice along these boundaries.

The equivalent positions in the crystal lattice of the PZT-based solid solutions (the substances under consideration) are occupied by ions with different sizes and/or different electric charges. In the bulk of each domain (away from the domain boundaries) the net force acting on each of these ions is zero. Near the interphase boundary the balance of forces is disturbed, and as a result the “large” ions are driven out into the domains with the larger configuration volume and correspondingly with the larger distances between atomic planes. At the same time the “small” ions are driven out into the domains with smaller distances between atomic planes. Such processes are accompanied by the competition of a reduction in the elastic energy along the interphase boundary on the one hand, and an increase of the energy caused by the deviation of the solid solution composition from the equilibrium composition on the other hand. The processes described above will be finished when the structure of the new interphase boundaries will correspond to the minimum of energy.

The *A*- and *B*-positions of the perovskite crystal lattice of the solid solutions are occupied by ions with different ionic charges (Pb^{2+}, La^{3+}, Li^{+} in *A*-sites and Zr^{4+}, Ti^{4+}, Nb^{5+}, Mg^{2+} in *B*-sites). Because of this the local decomposition of the solid solution along the interphase boundaries can be accompanied by the local disturbance of electroneutrality. Thus, the formation of the heterophase structure of coexisting domains is accompanied by a violation of the chemical homogeneity of the samples. At the same time, samples remain homogeneous at the temperatures above T_C, when dipole-ordered phases are absent.

2. Methods

Powder samples of the PZT-based solid solutions for our experiments were obtained by the co-precipitation of the components from the mixture of aqueous solutions of lead and lanthanum nitrates and chlorides of titanium and zirconium. After washing and drying the precipitates were annealed at 550 and 850 °C. Ceramic samples for studies of solid solutions were sintered at 1320–1340 °C. Transmission electron microscopy experiments were performed using JEM-200 electron microscope, accelerating voltage was 200 kV. Objects for TEM experiment had ~ (0.1–0.15) μm in thickness and was obtained by cleaving the ceramics crystal grains. The process of formation of segregates was controlled by the Debye–Scherrer x-ray method with using filtered Co *K*α radiation [13,14].

Samples for optical studies were manufactured by hot pressing method (at a pressure of 30 MPa) at 1250 °C for 8 h. Lamellae with the thickness of 0.3 cm were cut from the sintered bars. These lamellae were grinded and polished. Before polishing the grinded lamellas were annealed at 1200 °C in the presence of $PbZrO_3$ filling for one hour and after that at 1100 °C in oxygen enriched atmosphere during one hour. After the polishing the lamellae were subjected to the second annealing at 850 °C in oxygen enriched atmosphere for two hours. The wavelength dependences of the light transmission coefficient were measure using Hitachi U-4000 Spectrophotometer.

3. Results and Discussion

Manufactured PZT-based solid solutions had compositions corresponding to the state of the coexisting domains of the FE and AFE phases in the sample’s volume. The resistivity of prepared samples was of the order of 10^{16} Ω·cm.

The formation of segregates leads to appearance of the diffusive lines on x-ray patterns (marked by arrows on insert in Fig. 1). When the share of segregates in the sample’s volume increases, the intensity of diffusive x-ray lines grows also. Figure 1 demonstrates the duration of the decomposition process after quenching of the annealed sample from 600 °C. As it may be seen, the process of establishment of the equilibrium composite structure takes place during time interval up to 20–25 h.

The dips of the curves correspond to the presence of the negative refraction regime. The modulation depth can be controlled by changing the conductivity of segregates. It is also possible to select the optic wavelength range by changing the position of the solid solution in the “composition–temperature” phase diagram of the substance. Another possibility is by changing the position of the solid solution in the “electric field–temperature” phase diagram by means

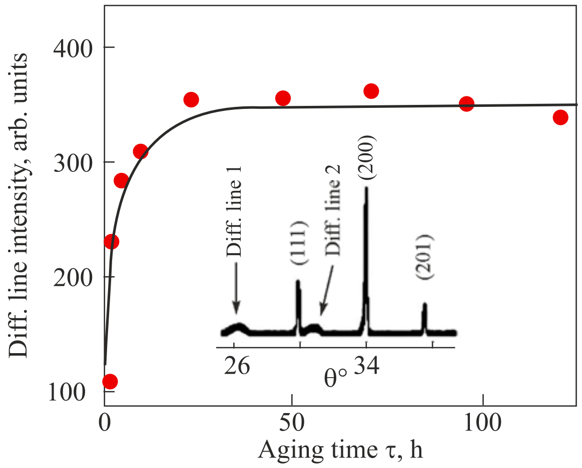

Fig. 1. Dependence of the diffuse line intensity on ageing time for the solid solution with the coexisting FE and AFE domains. The insert shows the x-ray Debye–Scherrer diffraction patterns obtained at the room temperature after the quenching and ageing of the sample for 30 days. The transparency of one of the discussed materials as a function of the wavelength for samples with different values of conductivity is presented in Fig. 2 as an example.

of varying the potential difference between the element's electrodes.

However, the most interesting results can be obtained using thin film structures. The change of the region of the negative refraction in this case can be achieved both by the application of the electric field to the film substrate (if the ferroelectric crystal is chosen as a substrate material) and by the flexural strains of the substrate. The modulation of the transmitted light has been observed in both these situations.

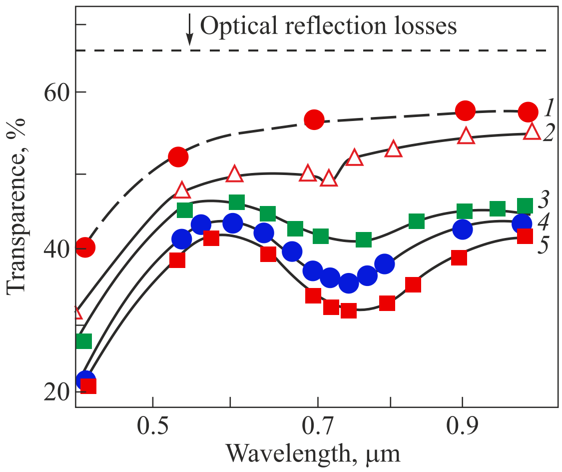

Fig. 2. Dependence of the light transmission coefficient on the wavelength for the transparent composite material (the dielectric matrix containing conductive metallic segregates). The increasing numbers near the curves correspond to the materials with increasing values of the conductivity of segregates.

4. Conclusions

Based on our results on use of the controlled decomposition of solid solutions for manufacturing of composite materials one can relatively easy manufacture the substances and device components with controlled optical characteristics. The present paper demonstrates the feasible way for manufacturing materials with the negative optic refractive index. For this purpose, we obtained composite structures dielectric–metal with the periodic arrangement of metallic inclusions. Such composite structure has been manufactures by means of the controlled decomposition of the solid solutions in the state when the coexisting domains of the AFE and FE phases are present in the solid solution volume.

The PZT-based solid solutions considered in this article are just an example of the substances suitable for manufacturing of such materials. Obtained structural composite represented a dielectric AFE matrix containing FE domains with a structure of conducting interphase boundaries separating domains of the FE and AFE phases. The electric conductivity of the interphase boundaries occurred as a result of the local decomposition of the solid solutions in the vicinity of these boundaries. Solid solution decomposition has been controlled by means of external influences such as the external DC electric field, pressure, and ion substitutions. Dimensions of the said metallic inclusions were from 8 to 12 nm, the periodicity of their arrangement were from 0.2 to 2.0 μm.

It has to be noted that there exists a series of studies [21–25] devoted to the conductivity of domain walls in ferroelectric and magnetoelectric thin films. In particular it has been demonstrated [21] that the 180° domain walls in ferroelectric tetragonal PZT may be conducting. Authors of Ref. 21 attributed the mechanisms leading to domain wall conductivity to defects interacting with partially charged domain walls. They also suggested that there is potential possibility of control of these mechanisms by strain and electrostatic boundary conditions.

The main distinguishing feature of domain walls considered in all above cited studies and our case is that in our samples the domain walls are the boundaries separating different phases (AFE and FE) and, thus, they have a different internal structure as well as different types of mechanisms leading to their conductivity. Moreover, mechanism considered in Refs. 21–25 is bound with existence of bottom conducting electrode. This is not necessary in our case.

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Тверді розчини зі співіснуючими фероелектричною та антифероелектричною фазами для створення нових матеріалів

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Контрольований процес розпаду твердих розчинів поблизу міжфазних меж, що розділяють домени співіснуючих антифероелектричних та фероелектричних фаз, відкриває нові області застосування для цих матеріалів. Тверді розчини на основі цирконата–титаната свинцю розглядаються як приклад речовин, придатних для створення матеріалів з від’ємним показником заломлення. Виготовлені композити являють собою діелектричну антифероелектричну матрицю зі структурою провідних міжфазних меж, що розділяють домени фероелектричної та антифероелектричної фаз. Електропровідність міжфазних меж виникає внаслідок локального розпаду твердих розчинів поблизу цих меж. За допомогою зовнішніх впливів можливо контролювати процес розпаду і, таким чином, провідність міжфазних меж.

Ключові слова: фероелектрик, антифероелектрик, фазове співіснування, локальне розкладання, наноструктура, від’ємний показник заломлення.