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Materials with ferro-antiferroelectric phase transition intented for energy accumulated and converting devices

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Considered are the results of development of materials for energy accumulating and converting devices. Requirements to such materials are formulated. Investigated is one of the directions for raising their efficiency which implies increase of electric strength.

Рассмотрены результаты разработки материалов для энергоаккумулирующих и энергопреобразующих устройств. Сформулированы требования к таким материалам. Исследовано одно из направлений повышения их эффективности, включающее повышение диэлектрической прочности.

The basic operating principle of ferroelectric (FE) energy accumulating and converting devices consists in accumulation of electric energy in the process of polarization followed by its release to a load resistance at depolarization. Application of electric field polarizes the working elements and those accumulate electric energy at the density $P_r^2/2\bar{\varepsilon}$, where P_r is the remanent polarization, $\bar{\varepsilon}$ is the average permittivity value in the course of polarization [1]. Such accumulators differ in the principle of depolarization process realization, i.e. by the way the accumulated energy is released. The simplest way is the phase transition into a non-polar state, namely, paraelectric (PE) or antiferroelectric (AFE) one. These transitions may be realized due to effect of temperature or mechanical stresses. The work principles and examples of practical application of the converters where the driving force of the depolarization process is temperature are presented in [2].

Most advanced are investigations and developments of the devices where the accumulated energy is released due to the action of pulsed mechanical load (impact). To obtain electric pulses at a power up to 1000 kW and higher, polarized FE materials are used. Under pulsed mechanical load, the polarized materials show both piezoelectric and ferroelectric properties. However, due to piezoelectric effect, there may be released electric energies of the order of $2\cdot10^4$ J/m^3, whereas due to depolarization of FE, the energies of 10^6 J/m^3 and more are achieved [3, 4]. Shown in Fig. 1 are the dependences of the voltage on ceramic working element electrodes and active load current. These data allow to estimate the electric parameters which may be obtained when using FE energy converters [4].

As a material for the converter working elements, lead zirconate-titanate (PZT) solid solutions are conventionally used. The phase diagram "composition — temperature" of these solid solutions is presented in Fig. 2 [5]. At first, the solid solutions were used located in the region of the morphotropic phase boundary (with approximately equal molar fractions of lead titanate and lead zirconate). These substances are characterized by the phase transition into PE state under mechanical loading. In this

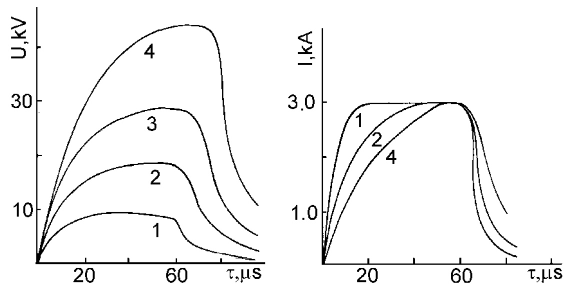

Fig. 1. Time dependences of the voltage on the ceramic working element electrodes and active load current. R_{load}, Ω: 1.02 (*1*), 5.96 (*2*), 8.90 (*3*), 10.0 (*4*).

case, the value of the energy released to load resistance is limited due to depolarization caused by instability of the domain structure which occurs long before the phase transformation itself. This results in an essential decrease of the effective P_r value and premature leakage of electric charge [1, 6–9]. Such materials have not found practical application.

Utilized in practice are the converters where the energy accumulated in a FE is released at the phase transition into AFE state. Materials with such phase transformations (PT) are most suitable for devices under consideration due to the following factors. In these materials, the accumulated energy has a maximum value. In particular, for $Pb(Zr_{0.965}Ti_{0.035})O_3$ + 1 mol% Nb_2O_5, $P_r = 38$ μC/cm^2 and $\varepsilon = 250$ and the accumulated energy density is 3.3 J/cm^3, whereas for $Pb(Zr_{0.525}Ti_{0.475})O_3$ solid solution from the morphotropic region, P_r = 35 μC/cm^2, $\varepsilon = 1250$ and the accumulated energy density is 0.7 J/cm^3. Accordingly, in the former case, the released energy density is higher: 1.8 J/cm^3 for $Pb(Zr_{0.965}Ti_{0.035})O_3$ + 1 mol% Nb_2O_5 and 1.4 J/cm^3 for $Pb(Zr_{0.965}Ti_{0.035})O_3$ + 1 mol% WO_3 solid solutions (these data correspond to quasi-static regime of the working element loading). Such energies are two or three times as high as those obtained while using the solid solutions belonging to the morphotropic region of the phase diagram [1].

However, even if the materials with FE-AFE transitions are used in the accumulator-converter working elements, only a certain part of the accumulated energy can be effectively used. In the case of shock-loading regime (used in real converters), this magnitude is considerably lower; it is defined by the electrical strength of the material. The problems associated with electrical breakdown of the working elements are considered in most detail in [6]. As a shock wave is passing through the working element, its resistance at the wave front changes crucially. For instance, at a shock amplitude of the order of 2·10^3 MPa, the estimated resistance of the 95/5 PZT ceramics is 10^2 Ohm·cm, that of barium titanate ceramics, 10^4 Ohm·cm, whereas in unloaded state their resistance lies within the interval 10^{10}–10^{12} Ohm·cm. Such an essential conductivity increase is connected with leakage currents caused by the charge released at the shock wave front.

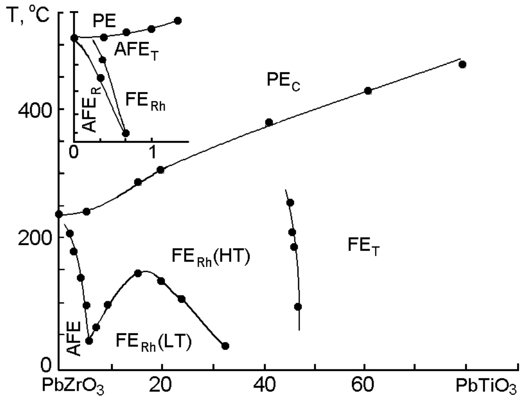

Fig. 2. Lead zirconate-titanate phase diagram after [5].

In Fig. 3, presented are the dependences of the electrode voltage of the 95/5 PZT ceramic working elements on the shock pulse amplitude. The working elements are polarized up to 10, 20 and 30 μC/cm^2. The residual polarization value defines the value of accumulated electrical energy. As seen from the Figure, irrespective of the initial polarization value, electrical breakdown occurs practically at the same electrode voltage about 5 kV/mm. The breakdown does not allow to realize the whole of the energy accumulated at polarization. In the experiments under discussion, it was only at 10 μC/cm^2 polarization extent that the whole of the accumulated energy could be released to load resistance.

The analysis shows that materials for the working elements of energy accumulating and converting devices must satisfy the following criteria:

1) the presence of FE-AFE PT under mechanical stresses;

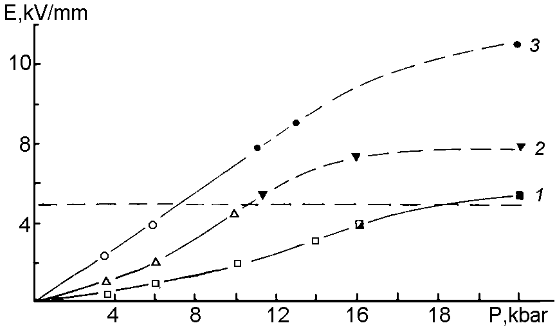

Fig. 3. Dependences of the electrode voltage of the 95/5 PZT ceramic working elements on the shock pulse amplitude P_r, μC/cm^2: 10 (*1*), 20 (*2*), 30 (*3*). Black points correspond to electric breakdown of working element.

2) the PT occurring at pressures lower than those which correspond to the domain disorientation;

3) high electrical strength;

4) easy production and a low cost.

Among the existing materials, PZT ceramics met the above-said requirements. It should be noted that it is not necessary to achieve extreme values of residual polarization and permittivity. It is just the electrical strength that defines the efficiency of the working elements most adequately.

When developing ceramic FE materials, much attention is paid to decrease of sintering temperature. As a rule, this is achieved by introduction of the so-called technological additives into the basic solid solution. Among such additives one can choose those having negligible influence on the residual polarization and permittivity. Therefore, in what follows, we shall consider the influence of such additives on the electrical strength of ceramic PZT materials. The main investigations were carried out on the samples of the 93/7 PZT solid solution. The doping was realized by both individual oxides and their complexes. Fig. 4 presents the dependences of the key working element parameters (the residual polarization P_r, dielectric permittivity ε and electrical strength E_{st}) on concentrations of individual oxides; the dependences of the same parameters on the sintering conditions are presented in Fig. 5.

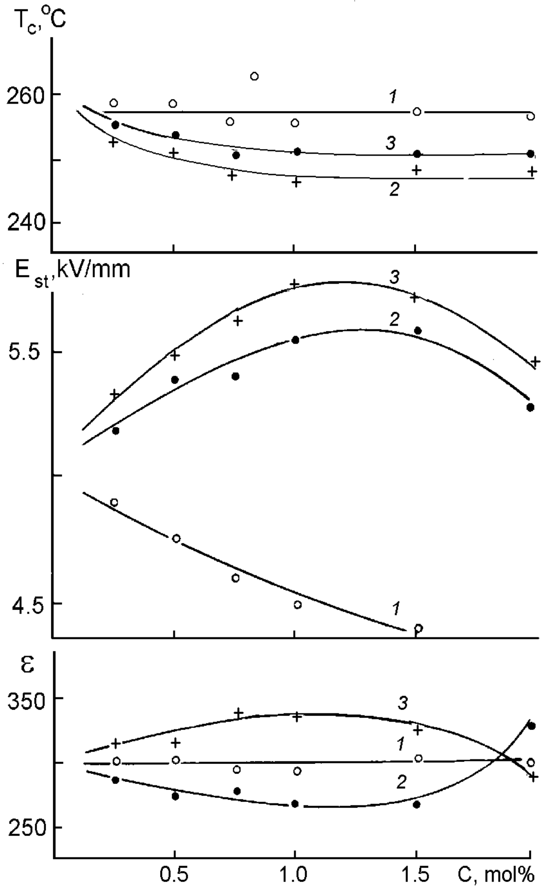

Fig. 4. PZT ceramic 93/7 parameters vs doping elements content: Co_3O_4 (*1*), V_2O_5 (*2*), CdO (*3*).

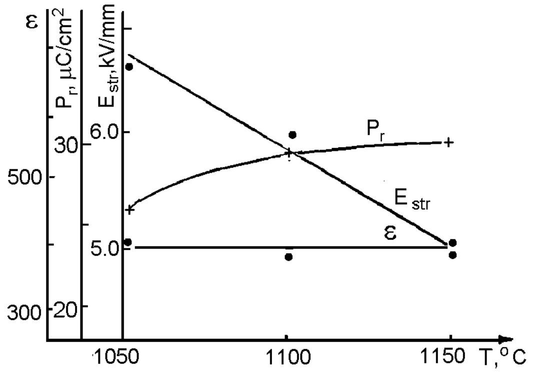

Fig. 5. PZT ceramic 93/7 parameters vs sintering temperature.

As seen from Fig. 4, the doping oxides may influence either all the mentioned parameters or only some of those, the others parameters remaining unchanged. The character of such an influence depends on the doping oxide type and its content in the solid solution. For instance, for CdO and V_2O_5 oxides, the values of all the parameters depend on the oxide content and the character of this dependence changes at $x \approx 1.0$. The dependences $E_{st}(x)$ contain bends corresponding to this content of doping oxides, the dependences $T_s(x)$ reach saturation, and at further increase of the doping oxide content, the Curie point of the solid solutions remains unchanged. The ceramic grain size shows opposite behavior: up to $x \approx 1.0$ it remains practically unchanged, whereas at higher oxide contents, the grains become noticeably smaller. When PZT solid solutions are doped with cobalt oxide Co_3O_4, the T_s and ε values do not depend on the additive content, whereas the breakdown voltage decreases noticeably and the grain size diminishes starting from small x values.

The micro-distribution of the elements in the ceramics volume was studied on the samples containing the same monoxides in amounts of 0.5 and 2.0 mol%. It is found that when the solid solution is doped with cadmium and vanadium oxides (0.5 mol%), the intensity of X-ray lines corresponding to the elements of the main solid solution (Pb, Ti, Zr), as well as to the doping elements, decreases at the grain boundaries. Microstructure investigation performed using microanalyzer scanning microscope in characteristic emission of each element shows decrease of brightness at the grain boundaries, whereas inside the grains, the brightness remains practically constant. At doping with the same amounts of cobalt, the latter "precipitates" in the inter-crystalline space and is almost absent in the ceramic grains. In the case of doping with all the mentioned oxides in amounts of 2 mol %, their "precipitation" in the inter-crystalline space takes place, too. The results obtained show that CdO and V_2O_5 oxides in amounts up to 1 mol% are dissolved in solid PZT solution, while at contents higher than 1 mol% they "precipitate" in the inter-crystalline space. Comparison of the $E_{st}(x)$ dependences with other concentration dependences shows that the material electrical strength becomes deteriorated noticeably when the content of doping elements is higher than their solubility limit in the solid solution.

The problem of the sintering temperature decrease acquires a particular significance in development of materials on the base of PZT solid solutions. This is caused by volatility of lead oxide at high temperatures which necessitates the special technological procedures for sintering at temperatures of 1100°C and higher. As a rule, the sintering temperatures are lowered using special additives. We studied the influence of different oxide complexes on the parameters of the sintered ceramics and investigated the ceramics sintering kinetics. The whole body of the obtained results is somewhat beyond the frames of the present work. Here we only emphasize that, as in the case of doping with monoxides, "precipitation" of the doping additive in the intercrystalline space results in decrease of the material electrical strength. At the same time, properly chosen technological additives which lower the sintering temperature may also allow to achieve a higher electrical strength than in the case of doping with monoxides. We have managed to obtain the materials with a residual polarization of 30 $\mu C/cm^2$ and permittivity of 250–400 with electrical strength reaching 10 kV/mm and more.

Though the use of technological additives permits to lower essentially the sintering temperature for ceramic materials, it is impossible to exclude completely the lead oxide volatilization and to avoid deviation from the composition stoichiometry. We have studied how non-stoichiometry of the main components of the solid solution influences its parameters, in particular, electrical strength. The following results have been obtained. Excess of any major component results in a noticeable lowering of electrical strength. At the same time, deficiency in zirconium or titanium up to 10 % does not effect the electrical strength of the ceramic samples and decreases their residual polarization and permittivity only slightly. As in the case of doping of the main solid solution with different additives, under such conditions "precipitation" of the surplus elements in the intercrystalline space causes a decreased electrical strength. Consequently, the efficiency of the material utilized in energy accumulating and converting devices becomes lower.

Thus, the experiments show that the sintering temperature variations, the "contamination" of the intercrystalline space (e.g. due to isolation of the impurities from the crystallites at increasing sintering temperature or sintering duration) results also in a decreased electrical strength of the material. The results obtained testify that the "precipitation" mechanisms of the impurities in the intercrystalline space are critical factors which define the electrical strength of PZT-based FE ceramics. The technological parameters must be chosen so that "contamination" of the inter-crystalline space will be minimal.

On the other hand, introduction of the doping elements into the crystal lattice results in shifting of the solid solution in the phase state diagram and in change of the mechanical factors which induce AFE PT. All the above-said shows that development of the materials for pulsed energy accumulating and converting devices is a tedious problem.

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Матеріали з феро- антифероелектричним фазовим переходом для пристроїв акумулювання та перетворення енергії

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Розглянуто результати розробки матеріалів для енергоакумулюючих та енергоперетворюючих пристроїв. Сформульовано вимоги до таких матеріалів. Досліджено один із шляхів підвищення їх ефективності, який включає підвищення діелектричної міцності.