

ON INFLUENCE OF STRUCTURE OF PIEZOELECTRIC PHASE ON PYROELECTRIC PROPERTIES OF POLYMER-PIEZOELECTRIC COMPOSITE

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It is shown, that the value of residual reorientation of polarization, in main, stipulated by domains which are distinct from 180° , their sizes and mobility determine pyroelectric properties of composites. The piezoelectric ceramics with high activation energy of domain walls and with a coefficient of uniform deformation of a crystal lattice are less effective as piezophase for pyroelectric composites.

By numerous researches of pyroelectric properties of composites on the basis of polar and non-polar polymers (matrix) and piezoelectric ceramics (disperser) of various structure it was shown earlier, that the pyroelectric effect in these heterogeneous systems is stipulated by residual domain-orientation polarization in the filler particles compensated by a charge stabilized on the polymer-piezoelectric ceramics phase boundary [1,2]. In this connection it is necessary to find out from what structural parameters of disperser particles the value of domain-orientation polarization for the pyroelectric effect, after their thermopolarization depends on.

As the structural parameters it is possible to accept a number of possible directions (N) of a vector of spontaneous polarization, a mobility of domain walls, a value of residual reorientation (P_r) and spontaneous (P_s) polarization, a degree of domain reorientations which are distinct from 180° (η , in %), a coefficient of a homogeneous deformation of a crystal lattice (δ) and sizes (μ) of grains (domains) in piezoparticles.

Rostov) in dependence of their position with respect to a morphotrope region (MR) is represented. It is seen, that η , P_r and δ by approaching from the part of rhombohedral region (R_h) to MR and by going away from it into tetragonal (T) region vary by a complex law. However, values of η and P_r in a case of rhombohedral structure are larger, in comparison with one's of tetragonal structure ceramics. A value of the parameter δ in the case of rhombohedral structure is noticeably less, than in the case of ceramics of tetragonal structure. A number $N=8$ for ceramics of rhombohedral structure, $N=6$ for ceramics of tetragonal structure and $N=14$ for ceramics of morphotrope region.

It is known, that the reorientation polarization P_r is a part of spontaneous polarization P_s of domains of crystal grains and is determined by a collection of all domain rotational displacements accomplished during polarization of ceramics [3]. At realization of all possible rotational displacements the reorientation polarization is maximum, thus its value depends on N in different phases. So, for a piezoelectric ceramics of the set PZT in rhombohedral and tetragonal phases the ratio P_r/P_s is equal 0,866 and 0,831, accordingly. In the case of existence of two phases, i.e. for R_h+T $P_r/P_s=0,922$. However the indicated number N is not a defining one for the value P_r , since practically at strong polarizing fields not all possible domain rotational displacements are implemented. The residual domain reorientations, accomplished during polarizations distinct from 180° bring the major contribution into the value of P_r and reaches the maximum value in a rhombohedral phase (fig.1).

Let us consider a connection of the structural characteristic of η piezoparticle with a pyroelectric coefficient γ and P_r of the composite. At realization of all possible domain orientations in piezoparticles during their polarization the value of the maximal P_r is in tetragonal ceramics

$$P_r = \left(\frac{1}{3} + \frac{2}{3} \eta \right) 0,831 P_s \quad \text{and in rhombohedral ceramics}$$

$$P_r = \left(\frac{1}{4} + \frac{3}{4} \eta \right) 0,866 P_s. \quad \text{Into the total value of } P_r \text{ the}$$

domains, which direction coincides with strength of polarization E_p , 180° domains and domains, which are distinct from 180° contribute. As it is known, the domains distinct from 180° , which determine are more mobile. They, as it seems, determine, mainly, pyroelectric properties of composites as a whole. Really, in the pyroelectric composites with piezoparticles possessing high value of η , the value of

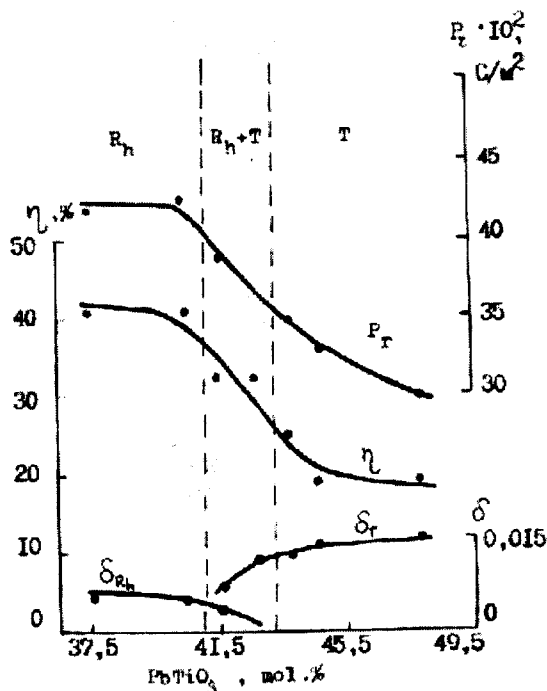


Fig.1. Dependences of η , δ and P_r on the content of $PbTiO_3$ in the $PbTiO_3$ - $PbZrO_3$ - $PbNb_{2/3}Zn_{1/3}O_3$ - $PbN_{2/3}Mg_{1/3}O_3$ system.

In fig.1 the change of some structural parameters of piezoelectric ceramics of the set PCR (piezoelectric ceramics

pyrocoefficient is larger, than in similar composites with the piezoparticle with smaller value of η .

Other important structural parameter is δ . This parameter characterizes the value of mechanical tensions originating at domain reorientations. The less, the closer a unit cell form to a cubic one and that is less energies are expended on mechanical deformations during the reorientation of domains. It is clear, that the decrease of δ means an increase of mobility of domain boundaries, and consequently, an increase of a value residual reorientation polarization (fig.1). From fig.1 it is visible, that by approaching a morphotrope region on the part of rhombohedral structure the value of P_r decreases.

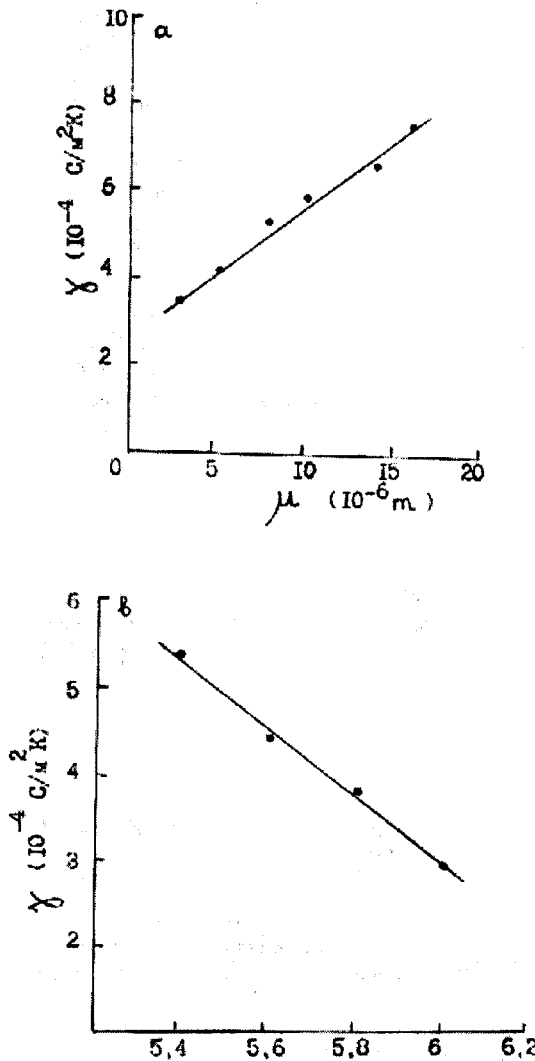


Fig.2. Dependences of pyrocoefficient γ on grain sizes μ of PVDF+PCR-8 (a) and PVDF+PCR-5 (b) composites.

In multicomponent ceramics such as PZT, utilised by us as fillers in composites, the structural parameter η decreases at transition from a rhombohedral phase into tetragonal and δ increases. These both parameters have various influence on the pyrocoefficient: the increase η means decrease of a number of domain boundaries which are distinct from 180° and it leads to an increase of the pyrocoefficient: the increase of δ leads to the decrease of a mobility of domain walls and to the decrease of the pyrocoefficient. Therefore composites with the ceramics of rhombohedral structure having the low

value of δ and the high value of η have more high pyrocoefficient than composites with the ceramics of morphotrope and tetragonal structures. In this case, in the tetragonal phase the main role is played by the decrease of the mobility of domain walls as a result of a growth of δ and in rhombohedral – the decrease of a number of domain boundaries as a result of a growth of η .

This proves to be true by the following experimental fact. It is known, that the ceramics of rhombohedral structure have more coarse domain structure with smaller number of domain boundaries in comparison with ceramics of tetragonal structure.

The grain sizes μ in the ceramics of rhombohedral structure can be changed over a wide range (from a several micron to a several tens of micron), while as in the ceramics of tetragonal structure μ varies in the range of several microns [3,4]. The increase of the grain size should result in increase of η and therefore, in increase of a pyrocoefficient, as it is observed experimentally for composites with the ceramics of rhombohedral structure. For example in fig.2 the dependence of pyrocoefficient of PVDF+PCR-5 composite on the grain size of the ceramics is presented. For the final solution of this problem the composites with the piezoelectric filler having tetragonal structure depending on grain size were investigated. For composites with ceramics of tetragonal structure the opposite pattern is observed – with an increase of grain size the pyrocoefficient decreases. As it is shown on fig.2,b the dependence of γ on μ for PVDF+PCR-8 composite can be explained by the fact to that in the case of tetragonal structure the change of the parameter η with change μ is practically insignificant and weakly influences on η of composite, and the crucial factor here is the parameter δ , that increases with an increase of grain size [3].

Thus, composites with rhombohedral structure have maximum pyrocoefficient in which the values of δ and η are high. It is known, that in a rhombohedral phase 180° , 109° and 71° domains exist, and in a tetragonal phase the same is true for 180° and 90° domains. Far from morphotrope region, both in rhombohedral and in tetragonal phases the behaviour of η and P_r of piezofiller is determined, in main, by the participation of 180° domains. By approaching morphotrope region from the part of tetragonal and rhombohedral phases in ferroelectric ceramics on the basis of PZT the walls not only 180° domains, but also 90° , 109° and 71° domains accordingly vibrate. It leads to noticeable growth of values of P_r and η . It is possible to estimate the energy of domain wall, which it will have, for example, on boundaries of morphotrope region. In this connection we shall use the known formula

$$W = 0,88P_r^2 d,$$

where P_r is a polarization inside domains, d is a constant of elementary cell, $d=4,08$ and $d=4,15$ Å for piezoceramics of rhombohedral and tetragonal structures, accordingly [3].

Therefore for the boundary of transition from a tetragonal phase in the smoothed (R_h+T) phase it is accepted, that $P_r=0,831P_s$, $d=4,115$ Å and for transition from rhombohedral to tetragonal phase $P_r=0,922P_s$, $d=4,08$ Å. The values of boundary their morphotrope region from the side of

R_h and T phases, are accordingly equal: $0,48 P_s^2$ and $1,01 P_s^2$ $\frac{J}{m^2}$. Such difference in values of energy of a domain wall of piezoceramics of the set PZT on boundaries of morphotrope region and on various distances from MR with the change of concentration of $PbTiO_3$, and also the difference of their crystallophysical and crystallochemical parameters contribute to the formation of residual reorientation polarization and pyroelectric characteristics in composites depending on the piezoparticle structure.

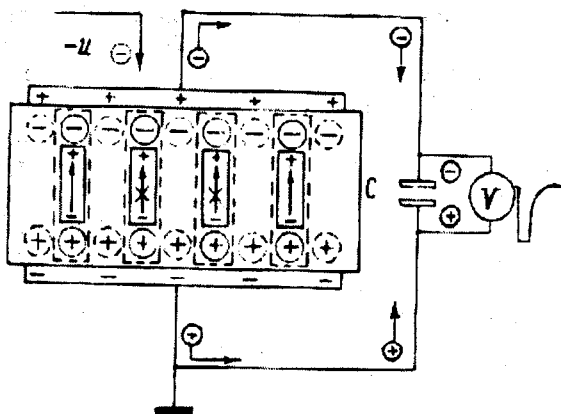


Fig.3. The model of the pyroelectric composite.

state will be formed in polymer-piezoelectric composites in the case when the piezoelectric phase has a high values of P_r and η , and the mobility of domain walls is high too.

Taking into account the above-mentioned conclusion, on the basis of model offered in fig.3 it is possible to explain the origin of the pyroelectric effect in polymer-piezoelectric composites as follows: due to injection of charges in piezophase and its electric conduction the oriented domain of piezoparticle are neutralized by free charge of the opposite sign and the effective charge defined as their difference, is equal to zero. Therefore, the presence of polarization outwardly does not appear. At heating the reorientation of domains occur, in main, the domains which are distinct from 180° and releasing part of the free charges supports a direct pyroelectric current as the function of temperature. Therefore, the origin of pyroelectric effect in polymer-piezoelectric composites can be connected with reorientation polarization of the composite under the change of its temperature. By cooling the orientation of domains in a field of the injected charges stabilized in various traps, in main, on the phase boundary of polymer matrix and piezoparticle and by that there is appear a pyroelectric current of a reverse polarity. These components of current arise at the expense of converted residual polarization. The increase of domain structure mobility and lowering of the Curie temperature should result in an increase of a pyrocoefficient. These conditions, naturally, are satisfied by piezoceramics of rhombohedral structure.

Thus, it is possible to consider, that the high pyroelectric

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POLİMER PYEZOELEKTRİK KOMPOZİTİN PİROELEKTRİK XASSƏLƏRİNƏ PYEZELEKTRİK FAZANIN STRUKTURUNUN TƏSİRİ HAQQINDA

Göstərilmişdir ki, əsasən 180° -dən fərqli domenlərin yaratdığı qalıq reorientasiya polarizasiyasının qiyməti domenlərin yürüklüyü və ölçüləri kompozitlərin piroelektrik xassələrini təyin edir. Domen divarlarının aktivasiya enerjisinə və kristallik qəfəsin yüksək birincins deformasiya əmsalına malik olan pyezokeramikalar piroelektrik polimer kompozitlər üçün pyezofaza kimi az effektivdir.

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О ВЛИЯНИИ СТРУКТУРЫ ПЬЕЗОЭЛЕКТРИЧЕСКОЙ ФАЗЫ НА ПИРОЭЛЕКТРИЧЕСКИЕ СВОЙСТВА КОМПОЗИТА ПОЛИМЕР-ПЬЕЗОЭЛЕКТРИК

Показано, что величина остаточной реориентационной поляризации, в основном, обусловленной доменами, отличных от 180° -ных, подвижность и их размеры определяют пирозлектрические свойства композитов. Пьезокерамики с высокой энергией активацией доменных стенок и коэффициентом однородной деформации кристаллической решетки менее эффективны в качестве пьезофазы для пирозлектрических композитов.