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Abstract

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SINGLE CRYSTALS OF FERROELECTRICS WITH LARGE NONLINEARITY

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It is known that the ferroelectric properties of various substances are most pronounced in single-crystal specimens. Therefore, the study of ferroelectric solid solutions in the form of single crystals is of great interest. In such substances, a small content of one of the components substantially changes the physical characteristics of the entire composition (^1), and this opens up possibilities for controlling the properties of ferroelectrics. For the practical use of ferroelectrics, their nonlinear properties are especially important.

Among ferroelectrics of the perovskite type, until recently the ferroelectric solid solutions $Ba(TiSn)O_3$ stood out for the greatest nonlinearity. T. N. Verbitskaya, on the basis of additions of tin dioxide to barium titanate, obtained ferroelectrics with sharply pronounced nonlinear properties—variconds, which have already found application in a number of branches of industry in the form of polycrystalline ceramics (^2). However, the indicated solid solutions in ceramic form do not possess rectangular hysteresis loops and have a comparatively low Curie temperature (70–80°), which limits the range of their application. Moreover, they cannot be used where, in the course of the circuit, single crystals are required. As for single crystals close in composition to variconds (^3), their nonlinearity proves to be no higher than the nonlinearity of polycrystalline specimens. Our attempt to bring the composition of $BaTiO_3$—$BaSnO_3$ single crystals closer to the so-called BK-2 (^2) did not lead to the desired results, since small additions of Cr_2O_3, which sharply increase the nonlinearity of polycrystalline specimens, unfortunately do not enter the crystal lattice.

Thus, the task of obtaining single crystals based on barium titanate with improved parameters remains topical.

We proposed growing ferroelectric single crystals from compositions that are solid solutions of $BaTiO_3$—$BaHfO_3$. Potassium fluoride was used as the solvent. The concentrations of the components and the temperature regime were selected on the basis of our data on the fusibility of the K_2F_2—$BaTiO_3$—$BaHfO_3$ system. The crystals were grown in a closed platinum crucible, in a furnace with a nichrome heater. The thickness of the grown plates varies depending on the cooling rate of the melt and ranges from 60 to 700 μ. The composition of the grown crystals differs considerably from the compositions of the initial mixtures

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

for crystallization. Thus, with a content in the melt of 5 mol.% barium hafnate relative to barium titanate, only a small amount of barium hafnate entered the crystals, up to 1%; however, these small additions substantially affect the dielectric properties. The dielectric permittivity at the Curie point reaches, for them, a value of 15,000 at radio frequencies, and at the Curie point a sharp maximum is observed in the temperature dependence of ϵ. At

at room temperature $\varepsilon = 500$. The tangent of the dielectric loss angle at radio frequencies is comparatively small ($\operatorname{tg}\delta = 2 \cdot 10^{-2}$—$3 \cdot 10^{-2}$).

Small additions of barium hafnate have an especially strong effect on the nonlinear properties of the single crystals under study. This applies to various types of nonlinearity of the dielectric permittivity. Figure 1 shows the dependence of the dielectric permittivity on the electric-field strength at a frequency of 50 Hz. The increase in dielectric permittivity is more than 150-fold; the maximum, $\varepsilon = 140\,000$, is reached at $E = 1.1$ kV/cm.

Fig. 1. 1 –$BaTiO_3$; 2 –BK-2;
3 –$BaTiO_3$ –$BaHfO_3$

Fig. 2. 1 –alternating-field strength
($f = 1000$ Hz) 0.5 kV/cm; 2 –1 kV/cm; 3 –1.5 kV/cm;
4 –2 kV/cm; 5 –2.5 kV/cm

When the crystals are heated, the dielectric permittivity at the maximum increases, and the maximum is reached at a lower field strength. Figure 1 also plots the dependences of the dielectric permittivity of BK-2 ceramic (which has high nonlinearity) and barium titanate ceramic, taken from work ([2]), on field strength. If, as a characteristic of nonlinearity, one takes the ratio of the dielectric permittivity at the maximum ε_{max} to its value at small field strength ε_0 ($E = 0$), then, as follows from Table 1, the nonlinearity of the crystals we obtained is considerably greater than that of other compositions. For polycrystalline solid solutions $BaTiO_3$–$BaHfO_3$ ([4]), we did not observe such large values of nonlinearity.

Table 1

Fig. 3. Hysteresis loops of BaTiO3—BaHfO3 single crystals, f = 50 Hz, E = 10 kV/cm

Figure 3: Fig. 3. Hysteresis loops of BaTiO3—BaHfO3 single crystals, f = 50 Hz, E = 10 kV/cm

Composition	$BaTiO_3$	BK-2	$Ba(TiHf)O_3$ crystal
$K = \frac{\varepsilon_{\max}}{\varepsilon_0}$	5—6	20	> 100

To characterize the nonlinear properties of ferroelectrics, the dielectric permittivity is also studied under the simultaneous action of alternating and constant electric fields. As is known ([5]), the reversible nonlinearity N_p determines the degree of influence of a constant (biasing—

of the biasing field on the value of the reversible permittivity and is defined as $N_p = \frac{1}{\varepsilon_p}\frac{\Delta E_p}{\Delta E_=}$, where ε_p is the reversible dielectric permittivity, and $\Delta\varepsilon_p/\Delta E_=$ is its increment when the constant biasing field $\Delta E_=$ is changed. In this case the reversible permittivity is measured (by definition) in a weak field. If this definition of the nonlinearity coefficient is extended to the case of stronger alternating fields, which are encountered in practice, then the nonlinearity coefficient thus determined for the single crystals under consideration, $BaTiO_3$—$BaHfO_3$, is very large.

Fig. 3. Hysteresis loops of $BaTiO_3$—$BaHfO_3$ single crystals, $f = 50$ Hz, $E = 10$ kV/cm

Figure 2 gives the dependences of the dielectric permittivity on the constant biasing field for different values of the alternating-field voltage at a frequency of 1000 Hz. As follows from the figure, increasing the constant field to 3 kV/cm decreases the dielectric permittivity by a factor of 50. From the curves in Fig. 2, values of N_p were calculated that are greater than 2 (for individual crystals $N_p = 5$). For comparison, it may be noted that in $BaTiO_3$ single crystals at $E = 1$ kV/cm $N_p = 0.05$; for $Ba(TiSn)O_3$ crystals, close in composition to variconds, the nonlinearity coefficient at this same field strength does not exceed 0.25 ([4]).

Oscillograms of the hysteresis loops of $BaTiO_3$—$BaHfO_3$ single crystals have a high rectangularity (Fig. 3), with saturation already reached at fields of 5 kV/cm. A study of the current loops, i.e., the dependence of the current through the crystal on the field strength, showed that the differential permittivity of the crystal ε_d at the points of steep rise of the loop branches exceeds 500,000, which in turn characterizes the rectangularity of the loop. The coercive field strength is $E_k = 1$ kV/cm. The electrical conductivity of the crystals is small. At room temperature σ has a value on the order of $10^{-12}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$. On heating, the electrical conductivity increases and at a temperature of 250° already has a value of $10^{-8}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$. The crystals possess a large piezomodulus and are easily polarized.

It is characteristic that those crystals which possess large nonlinear properties also have large values of the piezomodulus.

Conclusions

1. The possibility has been shown of growing ferroelectric single crystals with a Curie temperature practically not differing from the Curie temperature of $BaTiO_3$, but having improved parameters. The latter is achieved by introducing small additions of $BaHfO_3$ into $BaTiO_3$ single crystals.
2. The crystals possess high nonlinear properties, which manifest themselves over a wider temperature range than for variconds, in which the Curie point lies within 70–80°.
3. At radio frequencies the crystals have a small dielectric loss angle.
4. The crystals are easily polarized, and the piezomodulus d_{33} is larger than for ceramic barium titanate.
5. It may be assumed that the improvement of the nonlinear properties and other substantial changes in the dielectric parameters are caused not so much by speci-

physical properties of the solid solutions $BaTiO_3$—$BaHfO_3$ as by changes during the crystallization and growth of the crystals caused by the presence of barium hafnate.

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REFERENCES

1. A. L. Khodakov, M. L. Sholokhovich, *Izv. AN SSSR, ser. fiz.*, **22**, 1445 (1958).
2. T. N. Verbitskaya, *Elektrichestvo*, No. 3, 68 (1960).

3. A. L. Khodakov, M. L. Sholokhovich, *Izv. AN SSSR, ser. fiz.*, **24**, 1238 (1960).

4. M. L. Sholokhovich, A. L. Khodakov, T. N. Lezgintseva, *Ferroelectrics*, Rostov-on-Don, 1961, p. 12.

5. L. M. Kazarnovskii, *Ferroelectric Ceramic Capacitors*, 1956.

Note: Figure translations are in progress. See original paper for figures.