NEW PIEZOELECTRIC CERAMICS

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Résumé. — De nouveaux matériaux piézoélectriques ont été réalisés, grâce aux moyens fournis par la chimie des cristaux pour faire croître les propriétés piézoélectriques des solutions solides dans le voisinage de la région morphotropique, et grâce aux conceptions sur l'influence des défauts de structure sur les processus de frittage des céramiques.

En étudiant les propriétés des solutions solides du système $PbTiO_3$-$Pb(Fe_{1/2}Nb_{1/2})O_3$, on a obtenu un matériau ayant d'importantes propriétés piézoélectriques ($\varepsilon \simeq 4\,000$, $d_{31} \simeq 7 \times 10^{-6}$ unités CGSE, $K_r \simeq 0{,}5$).

L'étude de l'influence des additifs sur les propriétés des solutions solides $PbTiO_3$-$PbZrO_3$ a permis de créer un grand nombre de nouveaux matériaux à hautes propriétés ($\varepsilon \simeq 1\,500$, $K_r \simeq 0{,}6$, $d_{31} \simeq 5 \times 10^{-6}$ unités CGSE, $Q_m \simeq 1\,500$).

La particularité de ces nouveaux matériaux est leur basse température de frittage, ce qui rend possible l'élargissement de la gamme de leurs applications.

Abstract. — New piezoelectric materials have developed on the base of the crystal chemistry conceptions of increasing the piezoelectric activity of solid solutions in the morphotropic boundary region and on the base of conceptions about influence of the defect structure on the process of sintering of the ceramics.

While studying the properties of the solid solutions in the system $PbTiO_3$-$Pb(Fe_{1/2}Nb_{1/2})O_3$, the material with high piezoelectric activity ($\varepsilon \sim 4\,000$, $d_{31} \sim 7 \times 10^{-6}$ CGSE units, $K_r \sim 0{,}5$) was obtained.

The investigation of the influence of additives on the properties of the solid solutions $PbTiO_3$-$PbZrO_3$ made it possible to create a number of new materials with high properties ($\varepsilon \sim 1\,500$, $K_r \sim 0{,}6$, $d_{31} \sim 5 \times 10^{-6}$ CGSE units, $Q_m \sim 1\,500$).

The distinguishing feature of the developed materials is low sintering temperature of ceramics (1 000-1 100 °C), which makes it possible to increase the range of its applications.

The piezoelectric materials of three types have acquired especial significance in modern technology [1], [2]. These are piezoceramics with high piezoeffect, piezoceramics with high mechanical quality factor and piezoceramics having stable electrical parameters in wide range of temperature, pressure and electric field. The materials of the lead zirconate — lead titanate (PZT) series are most perspective for these purpose. The electric properties of some PZT materials are known from literature [1], [3], but information on details of composition and technological procedures is often not available. In this report information is given concerning our recent research on creating new piezoelectric ceramic materials for various applications.

The investigation carried out were based on crystal chemistry conceptions about an increase of solid solution piezoelectric activity at the morphotropic phase boundary region [4], [5] and about structure imperfections influence on the sintering of ceramics [6]. Respectively there were two directions of investigation : the first, a search of new materials in the $PbTiO_3$-$Pb(Fe_{0.5}Nb_{0.5})O_3$ system and the second, improvement of properties and lowering of the sintering temperature of the PZT series ceramics by means of some small additions.

The solid solutions with perovskite structure and the existence of the tetragonal-rhombohedral morphotropic phase boundary were found in the system $PbTiO_3$-$Pb(Fe_{1/2}Nb_{1/2})O_3$ [7]. By modifying the solid solution of this system with lithium oxide, a ceramic material with high piezoeffect was obtained [8], [9]. The composition corresponding to the morphotropic phase boundary has high values of electromechanical coupling ($K_r \sim 0.5$), dielectric constant ($\varepsilon \sim 4\,000$) and piezoelectric modulus ($d_{31} \sim 7 \times 10^{-6}$ CGSE units). The Curie temperature is 120 °C.

The investigation of additives influence on the electrical and physical properties of the PZT solid solution series ceramics led to creation of new materials with high Curie temperature (over 300 °C), high electrical properties (ε over 1 500, K_r over 0.6 ; d_{31} over 4×10^{-6} CGSE units) and lower sintering temperature. The additives of germanium dioxide [10], [11] and more complex ones containing bismuth or boron were found to be moust effective. The electrical properties and compositions of some materials with high piezoeffect which are of the Pb(Fe, Nb, Ti)O_3 and Pb(Zr, Ti)O_3 series are shown in the table I.

To obtain the piezoelectric ceramics with high mechanical quality factor we investigated the effect of complex bismuth and manganase containing additives of composition $Bi(M^{2+}_{0,5}Mn_{0,5})O_3$ or

$$Me^{2+}(Bi_{2/3}Mn_{1/2})O_3,$$

where M^{2+} is Zn, Cd, Co, Ba, Sr on sintering and

TABLE I

The electrical properties of the ceramic materials with high piezoeffect

Nr	T-sintering °C	ε	tg σ	T_k °C	K_r	$d_{31} \times 10^{-6}$ unit CGSE	Q mech	$E_y \times 10^{-12}$ unit CGSE
1.	1 000	4 500	0.010	120	0.50	7.4	130-160	0.65
2.	1 000	3 900	0.010	130	0.43	5.2	130-160	0.66
3.	1 050	1 500	0.020	310	0.50	4.5	80	0.77
4.	1 020	1 180	0.021	350	0.55	4.3	64	0.74
5.	1 080	1 450	0.020	325	0.60	5.0	57	0.69
6.	1 080	1 550	0.017	330	0.62	5.1	—	—

Composition of the Samples

1. $0.93\ Pb(Fe_{1/2}Nb_{1/2})O_3$ - $0.07\ PbTiO_3$ + 5 % mol. Li_2O
2. $0.92\ Pb(Fe_{1/2}Nb_{1/2})O_3$ - $0.08\ PbTiO_3$ + 5 % mol. Li_2O
3. $(Pb_{0.95}Sr_{0.05})(Zr_{0.53}Ti_{0.47})_{0.98}Ge_{0.02}O_3$ + 1 % W Nb_2O_5
4. $0.98\ Pb(Zr_{0.53}Ti_{0.47})O_3$ - $0.02\ Bi(Li_{1/3}Ge_{2/3})O_3$
5. $0.98\ Pb(Zr_{0.53}Ti_{0.47})O_3$ - $0.02\ Sr(Bi_{2/3}W_{1/3})O_3$
6. $0.98\ Pb(Zr_{0.53}Ti_{0.47})O_3$ - $0.02\ Sr(B_{2/3}W_{1/3})O_3$

TABLE II

The electrical properties of the ceramics materials with high mechanical quality factor

Nr 1	T-sintering °C	ε	tg σ	T_k °C	K_r	$d_{31} \times 10^6$ unit CGSE	Q mech	tg σ $E \approx 3$ kv/cm	TKF 10^6 1/grad. $-10 \div 50$ °C
1	1 060	550	0.005	340	0.50	2.4	1 400	⩽ 0.020	—
2	1 060	500	0.004	380	0.32	1.2	1 800	⩽ 0.015	20^+
3	1 060	850	0.005	340	0.55	2.9	1 150	⩽ 0.020	60^+
4	1 060	650	0.009	340	0.33	1.6	1 100	0.045	25^+
5	1 000	670	0.004	330	0.53	2.5	1 170	⩽ 0.020	200^+
6	1 060	550	0.015	> 300	0.41	1.9	550	⩽ 0.040	—

Composition of Samples

1. $0.98\ Pb(Zr_{0.53}Ti_{0.47})O_3$ - $0.02\ Zn(Bi_{2/3}Mn_{1/2})O_3$
2. $0.98\ Pb(Zr_{0.45}Ti_{0.55})O_3$ - $0.02\ Zn(Bi_{2/3}Mn_{1/2})O_3$
3. $0.98\ Pb(Zr_{0.52}Ti_{0.48})O_3$ - $0.02\ Bi(Zn_{1/2}Mn_{1/2})O_3$
4. $0.96\ Pb(Zr_{0.45}Ti_{0.55})O_3$ - $0.04\ Bi(Ni_{1/2}Mn_{1/2})O_3$
5. $0.98\ Pb(Zr_{0.53}Ti_{0.47})O_3$ - $0.02\ Cd(Bi_{2/3}Mn_{1/2})O_3$
6. $0.98\ Pb(Zr_{0.53}Ti_{0.47})O_3$ - $0.02\ Bi(Co_{1/2}Mn_{1/2})O_3$

properties of the PZT solid solutions at the tetragonal-rhombohedral morphotropic phase boundary. It was found that 2-4 mole percent of such additions were sufficient to lower the sintering temperature from 1 220-1 280 °C down 1 000-1 100 °C. The mechanical quality factor increased from Sr to Zn in series of Me^{2+} = Sr, Co, Cd, Ni, Zn. The properties of new materials obtained as a result of this investigation are represented in the table II.

Some of these materials have high temperature stability of resonance frequency wich is interesting for the filter technique. Some other ones have quite low dielectric power factor in high alternating electric fields alongside with high mechanical quality factor. With that the higher is the mechanical quality factor, the less is the dependence of the dielectric power factor on the electric field magnitude. This dependence is the least with the materials modified with the $Me^{2+}(Bi_{2/3}Mn_{1/2})O_3$ additives, where Me^{2+} is Zn or Cd.

For the property change with different influences of all the materials studied there is a distinction depending on the elementary cell distortion character. Thus the dependence of ε and tg δ on the electric field magnitude as well as the temperature dependence of resonance frequency are stronger for the samples with the rhombohedral distortion than for those with the tetragonal one.

References

[1] JAFFE (H.), BERLINCOURT (A. D.), *Proc. I. E. E. E.*, 1965, **53**, 1372.

[2] JAFFE (H.), *I. E. E. E. Trans.* Electron Devices, 1969, **6**, 557.

[3] *Physical Acoustics*, edited by W. P. Mason, 1964, **1A.**

[4] JAFFE (B.), ROTH (R. S.), MARZULLO (L.), *J. Appl. Phys.*, 1954, **25**, 809.

[5] VENEVTSEV (Ju. N.), BONDARENKO (V. S.), JDANOV (G. S.), CHKALOVA (V. V.), STREMBERG (N. G.), *Crystallogr.*, 1961, **6.**

[6] WEYL (W. A.), *Ceramic Age*, 1952, **II,** 28.

[7] DIDKOVSKAJA (O. S.), KLIMOV (V. V.), VENEVTSEV (Ju. N.), « *Izv. A. N. U. S. S. R., Neorgan. Materialy*, 1967, **3**, 1243.

[8] DIDKOVSKAJA (O. S.), KLIMOV (V. V.), VENEVTSEV (Ju. N.), *Avt. Svid. U. S. S. R.*, 26. 05. 1967, **222,** 480.

[9] DIDKOVSKAJA (O. S.), RUDENKO (T. P.), KLIMOV (V. V.) VENEVTSEV (Ju. N.), « *Electronnaja Technika*, 1969, **14**, 6.

[10] DIDKOVSKAJA (O. S.), SCHUKLINA (L. A.), KLIMOV (V. V.), VENEVTSEV (Ju. N.), *Avt. Svid. U. S. S. R.*, 212814. 24. 12. 1966.

[11] DIDKOVSKAJA (O. S.), DROBUSHEVA (L. A.), KLIMOV (V. V.), VENEVTSEV (Ju. N.), « *Electronnaja Technika* », 1969, **14**, 42.

[12] SAVENKOVA (G. E.), DIDKOVSKAJA (O. S.), KLIMOV (V. V.), VENEVTSEV (Ju. N.), BRONNIKOV (A. N.), *Avt. Svid., U. S. S. R.*, 9. 09. 1968, **268012.**