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Piezoelectric Ceramics for High Power Use

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Piezoelectric properties of $Pb(Zn_{1/3}Nb_{2/3})O_3$-$Pb(Sn_{1/3}Nb_{2/3})O_3$-$PbTiO_3$-$PbZrO_3$ quaternary ceramics are described. The ceramics exhibited high planar coupling coefficients and high dielectric constants. A small addition of MnO_2 to the quaternary ceramics increased markedly the mechanical quality factors Q_M and coercive fields E_c. The quaternary ceramics with combined addition of MnO_2 and Sb_2O_3 exhibited high planar coupling coefficient (0.56), high Q_M(2040), high E_c(19.5 kV/cm), high tensile strength and wide linear regions of piezoelectricity with dynamic stress.

§1. Introduction

Piezoelectric ceramics for high power use are extensively required to provide resonators for piezoelectric transformers, ultrasonic washing machines, sonar etc. It is necessary for piezoelectric ceramics for high power use to have high coupling coefficient, high mechanical quality factor, high coercive field, high mechanical strength and high durability with internal stress. The authors studied piezoelectric properties of $Pb(Zn_{1/3}Nb_{2/3})O_3$–$Pb(Sn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$–$PbZrO_3$ ceramics and obtained suitable ceramics for high power use.

§2. Experimental Procedure

The raw materials were PbO (purity 99.5%), ZnO(99%), SnO_2(99.8%), Nb_2O_5(99.8%), TiO_2(99.5%) and ZrO_2(99.5%). The additives used were chemical reagents. Weighed raw materials of a given composition were wet-mixed in a ball mill with agate balls, dried and calcined at 850°C for 2 hours. The calcined material was wet-ground, dried and pressed into discs (20 mm in diameter and 2 mm in thickness). The discs were fired at 1200 to 1310°C for 45 minutes in an electric furnace. The fired discs were lapped to a thickness of 1 mm, and silver paste was fired on both sides of the discs. Then the discs were poled in silicone oil at 100°C by applying a dc field of 4 kV/mm.

The dielectric constants $\varepsilon_{33}^T/\varepsilon_0$ and dissipation factors D were measured at 1 kHz. The piezoelectric properties were measured by a method similar to that of the IRE Standard.[1] The Curie point T_c was obtained from the measurement of temperature dependence for capacitance. Coercive field E_c was obtained from the measurement of the D-E hysteresis curve at 0.01 Hz. Maximum internal stress T_{max}[2] was calculated from the formula: $T_{max} = I_{max} \cdot \sqrt{\varrho}/(\sqrt{2}W.\, k_{31} \cdot \varepsilon_{33}^T)$, in which ϱ, W, k_{31} and ε_{33}^T were density, width of a bar specimen, coupling coefficient and dielectric constant, and I_{max} was the maximum current in which a change of resonant frequency by increase of current was −0.1%. The width of the linear region of piezoelectricity under dynamic stress depends on values of T_{max}. Therefore, ceramics having high T_{max} can be used in the conditions of high stress and power. The polished and etched surfaces of the ceramics were observed by using a scanning electron microscope.

§3. Results and Discussion

Recently, a great number of ternary ceramics consisting of $PbTiO_3$–$PbZrO_3$ and a complex perovskite type compound, i.e. $Pb(Mg_{1/3}Nb_{2/3})O_3$,[3] $Pb(Ni_{1/3}Nb_{2/3})O_3$,[4] etc. have been synthesized. These ternary ceramics exhibited high piezoelectricity. Piezoelectric properties of quaternary $Pb(Zn_{1/3}Nb_{2/3})O_3$ –$Pb(Sn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$–$PbZrO_3$ ceramics were investigated to obtain improved ceramics for high power use as compared with the above ternary ceramics.

Figure 1 shows $\varepsilon_{33}^T/\varepsilon_0$, k_p and Q_M of $Pb(Zn_{1/3}Nb_{2/3})_{0.09}(Sn_{1/3}Nb_{2/3})_{0.09}Ti_{1-D}Zr_DO_3$ ceramics, and shows that the ceramics having maximum $\varepsilon_{33}^T/\varepsilon_0$ (2212) and k_p (0.661) were obtained for compositions with D being

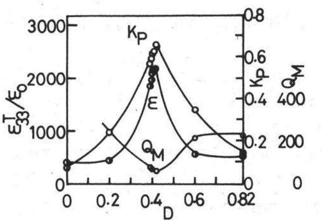

Fig. 1. $\varepsilon_{33}^T/\varepsilon_0$, k_p and Q_M of $Pb(Zn_{1/3}Nb_{2/3})_{0.09}(Sn_{1/3}Nb_{2/3})_{0.09}Ti_{0.82-D}Zr_DO_3$ ceramics.

0.42 and 0.415, respectively. Figure 2 shows N_p, T_c and E_c of the ceramics. The T_c and E_c of the ceramics decreased with increase of D. Frequency constants N_p exhibited a minimum in the ceramics with D of 0.415. The quaternary ceramics had high $\varepsilon_{33}^T/\varepsilon_0$ and k_p. However, the Q_M of the ceramics is too low to permit their use as ultrasonic vibrators for high power.

A previous article[5] has described the effects of MnO_2 additive on the piezoelectric properties of $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$–$PbZrO_3$ ceramics. Small additions of MnO_2 to the ceramics increased the Q_M. Therefore the effects of MnO_2 additive on the piezoelectric properties of the ceramics having the compositions of the present quaternary system were investigated.

Effects of MnO_2 additive on the piezoelectric properties of $Pb(Zn_{1/3}Nb_{2/3})_{0.09}(Sn_{1/3}Nb_{2/3})_{0.09}Ti_{0.42}Zr_{0.40}O_3$ ceramics are shown in Fig. 3. A small addition of MnO_2 increased markedly Q_M, E_c and T_{max}, and decreased $\varepsilon_{33}^T/\varepsilon_0$ and k_p. Figure 4 shows effect of MnO_2 additive on the grain size of the quaternary ceramics. The addition of MnO_2 enhanced to some extent the grain growth of the ceramics. Changes of resonant frequency and resonant resistance by the internal stress are shown in Fig. 5, and were very large at internal stress values of more than 80 kg/cm^2. The ceramics of Fig. 3 with 0.5 wt.%MnO_2 exhibited high Q_M along with high k_p and T_{max}.

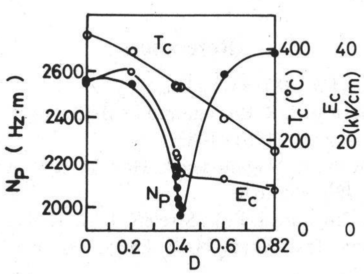

Fig. 2. N_p, T_c and E_c of $Pb(Zn_{1/3}Nb_{2/3})_{0.09}(Sn_{1/3}Nb_{2/3})_{0.09}Ti_{0.82-D}Zr_DO_3$ ceramics.

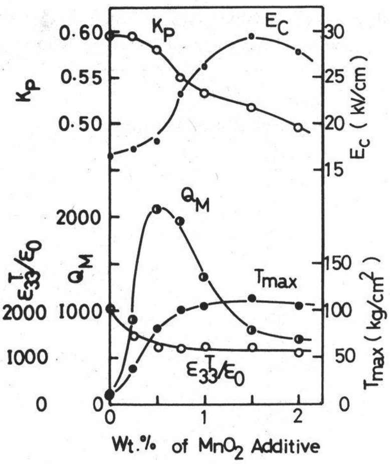

Fig. 3. Effects of MnO_2 additive on piezoelectric properties of $Pb(Zn_{1/3}Nb_{2/3})_{0.09}(Sn_{1/3}Nb_{2/3})_{0.09}Ti_{0.42}Zr_{0.40}O_3$ ceramics.

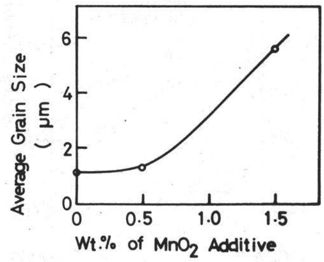

Fig. 4. Effect of MnO_2 additive on grain size of $Pb(Zn_{1/3}Nb_{2/3})_{0.09}(Sn_{1/3}Nb_{2/3})_{0.09}Ti_{0.42}Zr_{0.40}O_3$ ceramics.

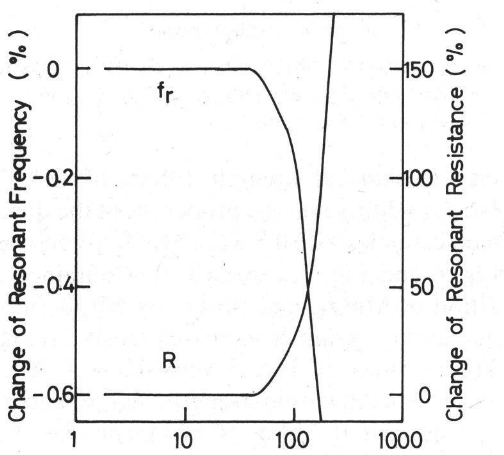

Fig. 5. Changes of resonant frequency (fr) and resonant resistance (R)—internal stress curves of $Pb(Zn_{1/3}Nb_{2/3})_{0.09}(Sn_{1/3}Nb_{2/3})_{0.09}Ti_{0.42}Zr_{0.40}O_3$ cearamics with 0.5 wt.%MnO_2.

Effects of certain additives on the properties of the quaternary ceramics with MnO_2 additive were investigated to obtain ceramics having

Table I. Electromechanical constants of $Pb(Zn_{1/3}Nb_{2/3})_{0.09}(Sn_{1/3}Nb_{2/3})_{0.09}Ti_{0.42}Zr_{0.40}O_3$ ceramics with combined addition of 0.5 wt.% MnO_2 and 0.5 wt.% Sb_2O_3.

Density (kg/m^3)	7800	d_{31} (10^{-12}m/V)	−124
Average grain size (μm)	1.7	d_{33} (〃)	271
T_c (°C)	281	g_{31} (10^{-3}V. m/N)	−10.2
E_c (kV/cm)	19.5	g_{33} (〃)	22.2
$\varepsilon_{33}^T/\varepsilon_0$	1380	s_{11}^E (10^{-12}m^2/N)	11.5
D (%)	0.5	s_{33}^E (〃)	13.8
k_p	0.56	Temperature coefficient of resonant frequency	
k_{33}	0.66	(10^{-6}/°C)	−24
k_{15}	0.63	Aging rate of resonant	
k_t	0.46	frequency	0.27
		(%/time decade)	
Q_M	2040	Tensile strength (before	550
σ^E	0.30	poling) (kg/cm^2)	

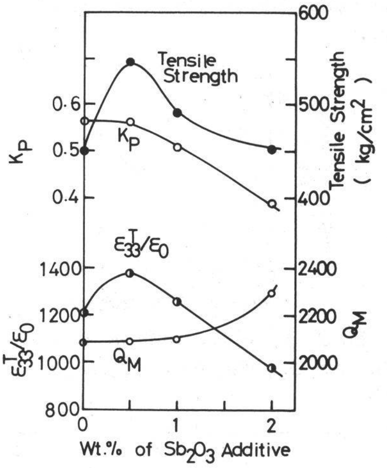

Fig. 6. Effects of Sb_2O_3 additive on the properties of $Pb(Zn_{1/3}Nb_{2/3})_{0.09}(Sn_{1/3}Nb_{2/3})_{0.09}Ti_{0.42}Zr_{0.40}O_3$ ceramics with 0.5 wt.%MnO_2.

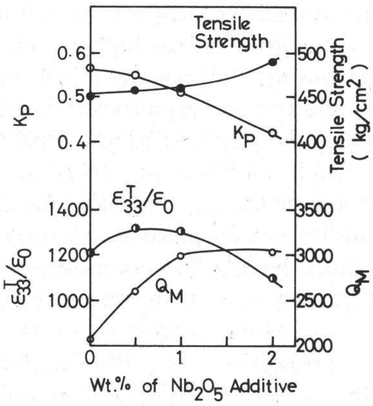

Fig. 7. Effects of Nb_2O_5 additive on the properties of $Pb(Zn_{1/3}Nb_{2/3})_{0.09}(Sn_{1/3}Nb_{2/3})_{0.09}Ti_{0.42}Zr_{0.40}O_3$ ceramics with 0.5 wt.%MnO_2.

high mechanical strength. Effects of Sb_2O_3 or Nb_2O_5 additive on the properties of the quaternary ceramics with 0.5 wt.% MnO_2 are shown in Fig. 6 and Fig. 7, respectively. Combined addition of MnO_2, and Sb_2O_3 or Nb_2O_5 to the quaternary ceramics increased tensile strength. The ceramics of Fig. 6 with 0.5 wt.% Sb_2O_3 exhibited high tensile strength, high E_c and high k_p, and had a value of 80 kg/cm^2 for T_{max}. Electromechanical constants of the ceramics are shown in Table I.

The ceramics of Table I have favorable properties for high power use, such as high coupling coefficient, high Q_M, high E_c, high mechanical strength and high durability with internal stress. The present ceramics can provide high power resonators for piezoelectric transformers, ultrasonic washing machines, etc.

§4. Conclusions

1) $Pb(Zn_{1/3}Nb_{2/3})O_3$–$Pb(Sn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$–$PbZrO_3$ quaternary ceramics exhibited high $\varepsilon_{33}^T/\varepsilon_0$ and high k_p.

2) A small addition of MnO_2 to the quaternary ceramics increased markedly Q_M and E_c.

3) Combined addition of MnO_2 and Sb_2O_3 to the quaternary ceramics increased tensile strength.

References

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