IMPACT COMPRESSION OF PIEZOCERAMICS

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We investigated the dynamic compressibility of a piezoceramic composed of lead zirconate-titanate (LCT) and its depolarization by shock waves over the pressure range 100-500 kbar. We also observed the changes that persisted in the specimens after brief compression at pressures of 350 and 500 kbar. The dependence of the piezocurrent on time was used to calculate the dielectric permeability and conductivity of the ceramic beyond the shock-wave front over the pressure range investigated. This article discusses the possibility of a phase transition to the paraelectric phase in LCT during compression by a shock wave.

In addition to the research on polarization of ionic crystals and other dielectrics in shock waves [1], studies have now been made of piezoceramics under dynamic conditions [2-7].

Detailed studies have been made of a piezoceramic based on lead zirconate-titanate (LZT or PZT), PZT 52/48, PZT 95/5, barium titanate, and certain other metals.* Dynamic studies in the low-pressure region have revealed two-wave configurations [3, 5]. The amplitude of the first wave amounts to 20-40 kbar and, as noted in the literature [5], depends to a material extent on the initial specimen density. This is related to the nature of the process involved in development of two-wave configurations, which are due to the influence of strength.

The depolarization of PCT 52/48 piezoceramic has been investigated [3], and it has been shown that the dependence of the electric charge liberated when a shock wave passes across the specimen on the pressure has a complex form. Study of the piezocurrent as a function of time at small shock-wave intensities (up to about 25 kbar) [6, 7] led to the conclusion that the conductivity of the impact-compressed ceramic becomes substantial at relatively low pressures, amounting to about $10^{-2}\ \Omega^{-1}\cdot\text{cm}^{-1}$. Examination of preliminarily polarized ceramic specimens after passage of shock waves carrying a pressure of up to about 25 kbar showed that a substantial proportion of the residual polarization is retained in some types of ceramics [4].

In the present investigation, we studied LCT 53/47 piezoceramic with the composition $\text{PB}_{0.95}\text{Sr}_{0.05}\cdot(\text{Zr}_{0.53}\cdot\text{Ti}_{0.47})\text{O}_3 + 1\%\ \text{Nb}_2\text{O}_5$. The dynamic compressibility was measured by the reflection method [9] over the pressure range 100-470 kbar. The piezocurrent and its change as a shock wave was passed across the specimen were measured over the same pressure range. In order to establish the irreversible changes caused by impact compression, we conducted experiments in which the specimens were examined under brief compression at pressures of 350 and 500 kbar, using the method described by Dulin et al. [10].

The experiments were conducted with ceramic specimens having a width of up to 20 mm and a thickness l = 2-3 mm. The initial specimen density was 7.3-7.4 g/cm^3. The faces of the specimens were covered with a layer of silver ~15 μ thick. The polarized ceramic was used in all the experiments. The initial polarization P_0, measured with the specimens heated to temperatures above the point T_0 = 305°C [8], amounted to 35 μC/cm^2, while the dielectric permeability (ε_0) was 1500.

1. Rectangular shock waves were set up by BB charges, which were separated from the test specimens by copper or aluminum screens. The wave velocities U in the piezoceramic were measured by the electro-

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*Data on the compositions and properties of LCT and PZT are given in the literature [5, 8].

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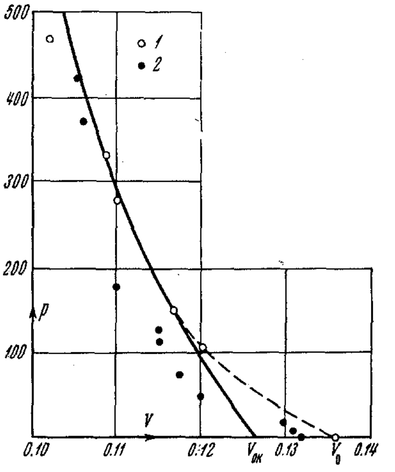

Fig. 1

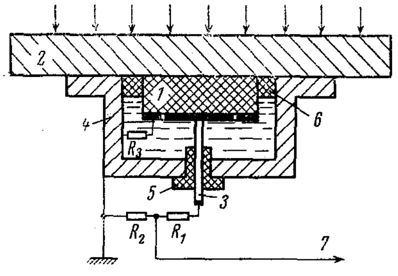

Fig. 2

TABLE 1

U, km/sec	u, km/sec	p, kbar	T, °C	Number of measurements
3.49±0.06	0.41	105	100	11
3.79±0.04	0.54	149	140	12
4.44±0.04	0.85	278	270	15
4.69±0.05	0.96	332	330	12
5.04±0.03	1.26	467	540	12

contact method [9]. The mass velocities u and pressures p were found from the measured values of U and the known dynamic adiabats of the screens; the shock-wave intensities in the latter were determined beforehand [11]. Table 1 presents the results obtained in measuring the dynamic compressibility of LZT 53/47 piezoceramic with a density $\rho_0 = 7.35$ g/cm^3; Figure 1 shows the same results plotted on the coordinates pressure (kbar) versus specific volume V (cm$^3 \cdot$g^{-1}) (points 1). At $p \leqslant 150$ kbar (Fig. 1), segments of the adiabat were interpolated for $\rho_0 = 7.9$ g/cm^3 (solid line) and $\rho_0 = 7.35$ g/cm^3 (dash line). For purposes of comparison, this figure also gives points 2 [3], which were obtained in investigating a ceramic with a composition similar to PZT 52/48.

As can be seen from Fig. 1, the data for the high-pressure region (~400 kbar) coincided but there was a discrepancy at pressures below 200 kbar, with a difference of about 4% in the specific volumes. In analyzing the data obtained, Reynolds and Seay [3] concluded that a two-wave configuration exists over the pressure region 20-230 kbar. This phenomenon was not observed over the pressure range 100-350 kbar in LZT 53/47 piezoceramic. This is demonstrated by the linearity of the U-u function; Table 1 gives the mean square deviations from the average for U. All the points on the dynamic adiabat (except the point at p = 467 kbar) are well described by the relationship $U = 2.62 + 2.16\,u$ (km/sec).

The discrepancy in the data on dynamic compressibility for the ceramics compared apparently resulted from differences in the composition and initial density of these materials.

If we neglect the thermal pressures, which are small and are estimated not to exceed 5% (the Grüneisen constant is about 0.5), the dynamic adiabat obtained for a porous material in the pressure region where strength defects are unimportant should also approximately describe the impact compressibility of a ceramic with a crystallographic initial density. At pressures below 150 kbar, the dynamic adiabat for a solid material can be obtained by interpolation (according to x-ray diffraction data, the crystallographic density of LZT 53/47 is 7.9 g/cm^3). The dash line in Fig. 1 represents the interpolated adiabat for a porous material at room temperatures.

We evaluated the temperatures along the impact adiabat in order to determine the pressures at which a phase transition from the ferroelectric to the paraelectric phase is possible in the ceramic in question. The calculated results are presented in Table 1. It was assumed that the isentropic line and the impact adiabat coincided from the point V_{0k} on the coordinates p versus V. The heat capacity was also assumed to be constant ($c_z = 0.16$ cal/g · deg).

2. Figure 2 is a schematic diagram of the experiments in which the current was measured during the passage of a shock wave over LZT 53/47 piezoceramic; this figure shows the specimen (1), the screen at which the plane impact wave is generated (2), the electrode (3), the metal beaker (4), the insulating sleeve

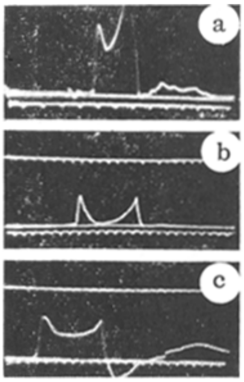

Fig. 3

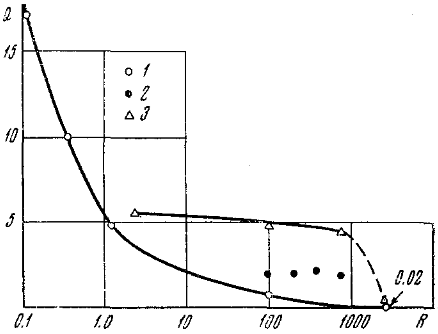

Fig. 4

(5), the centering ring (6), and the lead to the oscillograph (7). The central piezoceramic electrode was separated from the peripheral surface (retaining ring) by a gap of 0.15 mm. The ratio of the areas of the retaining ring and central electrode was 2 in most of the experiments. The resistance R_3 was accordingly half the load resistance R. The latter was determined from the values of R_1 and R_2 and the input resistance of the oscillograph (OK-17M or OK-21). The resistance R_1 was varied from 0 to 2.5 kΩ and R_2 was varied from 0.1 Ω to ∞.

In order to prevent electrical breakdown along the lateral surface of specimen 1, beaker 4 was filled with capacitor oil. The direction of the polarization sector was opposite to that of shock-wave propagation in almost all the experiments.

Figure 3 gives typical oscillograms, which show the manner in which the current pulse was deformed after R was increased at a pressure of 280 kbar; the load resistance was 50 (a), 400 (b), or 800 Ω (c). The scanning direction was from left to right. The time scale was 5 (a) or 10 (b and c) MHz.

The form of the current pulse depended on the pressure and the external load resistance and was also governed by the ratio between RC and the time, which was associated with the conductivity and dielectric permeability of the material beyond the shock-wave front. The maximum and subsequent minimum in the current occurred at the beginning of almost all the oscillograms. The same qualitative i(t) relationship was reported by Zel'dovich [12], who investigated the impact polarization of dielectrics; his phenomenological description was the same for impact depolarization of piezoceramics.

The theory of impact polarization of dielectrics has been the subject of work by a number of authors [12-15]. The problem was solved in its most general form by R. M. Zaidel' [15]. His hypothesis that a dielectric is linear and that the electric field has no effect on the state of the material ahead of the front can be applied to piezoceramics at high pressures.

The case of low shock-wave intensities (~ 10 kbar), where the change in polarization ahead of the wave front is large and the nonlinear effects become important, has been considered for ceramics [6, 7], but the appearance of volume free charges behind the wave front was neglected. The theory in question [6, 7] is therefore inapplicable to the pressures that occur above 20 kbar, where the increase in the conductivity of the compressed material begins to have a noticeable effect.

Measurement of the current during impact compression of a piezoceramic [6, 7] and observation of the residual polarization after passage of shock waves [4] confirm that the residual polarization almost completely disappears at pressures of ~30 kbar, i.e., we can assume $D = \varepsilon E$ beyond the shock-wave front (where D is the electrical induction, E is the field strength, and ε is the dielectric permeability, which is presumed to be constant). This assumption is valid at high pressures and is adopted in our subsequent discussions.

Figure 4 shows the charge $Q[\mu C/cm^2]$ moving through the circuit during passage of the wave over the specimen (0.5-0.8 μsec) as a function of the load resistance R (Ω); points 1, 2, and 3 correspond to pressures p of 467, 149, and 105 kbar. It can be seen from this graph that the change in the free charge on the ceramic electrode during the recording period was small and did not exceed 15% of the initial charge at loads ≥ 1 Ω (at which the measurements were made). It can therefore be assumed that the change in polarization ahead of the shock-wave front was small and that the electrical-induction function $D_1 = D_0 + \varepsilon_0 E$ is approximately linear for the material ahead of the wave front.

TABLE 2

p, kbar	$\varepsilon \cdot 10^{-3}$	$\lambda \cdot 10^{3}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$
105	4.3±0.4	4.5±0.5
149	4.6±0.4	6.6±0.9
278	9.6±5	22±2.5
332	11	40±15
467	—	100

Given these assumptions, Zaidel's solution [15] can be used without any modifications to calculate ε and λ (the conductivity) in the compressed material. Since the ceramic is nonconductive in its initial state, the equation for the current in a circuit with a resistive load is [15]

$$\alpha\tau \frac{di}{dx} + [k\tau + \alpha - (\alpha - 1)x]\, i + [k(1 - x) - (\alpha - 1)] \int_0^x i\,dx = \frac{P_0 U}{l}$$

$$\alpha = \frac{\varepsilon U}{\varepsilon_0 (U - u)}, \quad k = \frac{4\pi\lambda l}{\varepsilon_0 (U - u)}, \quad \tau = \frac{RCU}{l}, \quad x = \frac{tU}{l}$$

Here α characterizes the change in dielectric permeability, k is proportional to the conductivity of the compressed material, C is the initial capacity of the working portion of the specimen, x is the dimensionless time, and λ and ε are calculated with this equation from the maximum and minimum currents. As has been pointed out [12], the instants at which the extremal current values are reached are governed by the time τ (with $\alpha = 1$) and the time ($\sim k^{-1}$) required for appearance of volume charges in the compressed material, i.e., are directly related to the quantities λ and ε we are seeking.

Table 2 presents the results obtained in calculating the dielectric permeability ε and conductivity λ of the impact-compressed piezoceramic giving the average values of ε and λ for 4 or 5 experiments; the estimate $\varepsilon = 11 \cdot 10^3$ was obtained from the rise rate of the current; the estimate $\lambda = 0.1$ was obtained from the current amplitude at $\tau \approx 10\ l/U$. It can be seen from the data given that the conductivity of the compressed material was relatively large at p = 105 kbar and increased by a factor of about 20 when the pressure was raised to 470 kbar. The elevated temperature, which was estimated not to exceed 550°C over the entire range investigated, therefore is not sufficient to account for the high conductivity of the impact-compressed material (the conductivity in the normal state at these temperatures is $\sim 10^{-4}$–$10^{-5}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$). The increase in conductivity behind the wave front is apparently due largely to the characteristics of impact compression of the porous material.

As a check, we substituted the average parameter values from Table 2 into the initial differential equation. Solution of this equation by the numerical method yielded i(t) curves similar to the experimental curves.

The increase in the error in determining ε and λ as the pressure was raised was due to the decreasing characteristic time of conductivity (which governs the position of the current maximum) and consequently to the greater influence of shock-wave curvature and other distoring factors on the measurement results.

The maximum current was reached at x = 1 with large $\tau (> l/U)$. In this case, ε can be evaluated from the current rise rate and λ from the current amplitude at the end of the recording period. Table 2 gives some of the values obtained in this manner. They are less precise but they still agree with other data.

3. Experiments involving observation of specimens subjected to impact compression at pressures of 350 and 500 kbar were described in detail in a previous article [10]. Pressure was generated in the field blocks enclosing the test specimens (previously polarized) by the impacted plates propelled by explosion products. The piezoceramic specimens can be considered to have been subjected to single compression, since the steel and ceramics had almost the same dynamic rigidity. The pressure was relieved by a rarefaction wave following the shock-wave front by about 3 μsec.

The specimens exhibited a material change in density, from 7.35 to 7.7-7.8 g/cm^3. X-ray diffraction analysis showed that the crystal structure and lattice constants remained unchanged (to within 0.1%). Measurement of the residual polarization confirmed the impact compression completely depolarized the specimens and it can be assumed that the degree of depolarization by the shock wave increased with the pressure, starting at about 5 kbar [4].

4. In considering the transition of the initial tetragonal piezoceramic stage with ferroelectric properties to a paraelectric phase with a cubic structure, it must be taken into account that the Curie point decreases as the pressure rises. Thus, for a similar ceramic (PZT 52/48), $\Delta T_C / \Delta p \approx -0.7$°C/kbar, while this derivative is −4.2°C/kbar for barium titanate. Even assuming that the function $T_C(p)$ is less pronounced for the ceramic investigated (LCT 53/47), the data in Table 1 show that the transition to the paraelectric phase along the impact adiabat should occur at pressures not exceeding ~300 kbar.

Since the phase transition is accompanied by a change in compressibility, a singularity in the trend of the impact adiabat could be observed in the phase-transition region. Various transformations are usually manifested in inflections or "steps" in the curves representing the wave velocity versus the mass velocity, which are linear (with small parameter-variation intervals) if there are no abrupt changes in the compressibility of the material or discontinuous changes in specific volume. As was noted above, the experimental data were described by a linear U-u relationship at pressures below 330 kbar and the position at the point at 470 kbar indicates a substantial increase in compressibility. This result can be regarded as indicating that there is no phase transition during impact compression over the pressure range up to 300 kbar but that a transition is possible at pressures between 300 and 400 kbar.

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LITERATURE CITED

1. A. G. Ivanov, E. Z. Novitskii, V. N. Mineev, Yu. V. Lisitsyn, Yu. N. Tyunyaev, and G. I. Bezrukov, "Polarization of alkali halide crystals under impact loading," Zh. Éksperim. Teor. Fiz., 53, No. 1 (1967).
2. W. Neilson, "Effect of strong shocks in ferroelectric materials," Bull. Amer. Phys. Soc., 2, No. 6 (1957).
3. C. E. Reynolds and G. Seay, "Two-wave shock structures in the ferroelectric ceramics barium titanate and lead zirconate titanate," J. Appl. Phys., 33, No. 7 (1962).
4. R. K. Linde, "Depolarization of ferroelectrics at high strain rates," J. Appl. Phys., 38, No. 12 (1967).
5. D. G. Doran, "Shock wave compression of barium titanate and 95/5 lead zirconate titanate," J. Appl. Phys., 39, No. 1 (1968).
6. W. J. Halpin, Current from a shock-loaded shortcircuited ferroelectric ceramic disk," J. Appl. Phys., 37, No. 1 (1966).
7. W. J. Halpin, "Resistivity estimates for some shocked ferroelectrics," J. Appl. Phys., 39, No. 8 (1968).
8. I. A. Glozman, "Piezoceramic Materials in Electronic Engineering [in Russian], Moscow-Leningrad (1965).
9. L. V. Al'tshuler, "Use of shock waves in high-pressure physics," Usp. Fiz. Nauk, 85, No. 2 (1965).
10. I. N. Dulin, L. V. Al'tshuler, V. Ya. Vashchenko, and V. N. Zubarev, "Phase transitions in boron nitride during dynamic compression," Fiz. Tverd. Tela, 11, No. 5 (1969).
11. L. V. Al'tshuler, M. N. Pavlovskii, L. V. Kuleshova, and G. V. Simakov, "A study of alkali metal halides under impact compression at high pressures and temperatures" Fiz. Tverd. Tela, 5, No. 1 (1963).
12. Ya. B. Zel'dovich, "Emf produced during propagation of a shock wave through a dielectric," Zh. Éksperim. Teor. Fiz., 53, No. 1 (1967).
13. F. E. Allison, "Shock-induced polarization in plastics, 1. Theory," J. Appl. Phys., 36, No. 7 (1965).
14. A. G. Ivanov, Yu. V. Lisitsyn, and E. Z. Novitskii, "Polarization of dielectrics under impact loading," Zh. Éksperim. Teor. Fiz., 54, No. 1 (1968).
15. R. M. Zaidel', "Determination of electrical-relaxation regime during impact loading," Zh. Éksperim. Teor. Fiz., 54, No. 4 (1968).