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Hydrostatic Pressure-Forced Phase Transition from Ferroelectric to Antiferroelectric in Compositions of the $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3 + 0.8\% \text{WO}_3$ Type

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Abstract. Hydrostatic pressure acting on doped lead titanate-zirconate materials with a considerable proportion of zirconium induces a phase transition between ferroelectric and antiferroelectric states, which causes the previously poled specimens to depolarize. Measurements using a capacitance and those made on short-circuited specimens allow us to draw phase diagrams of the following types: "pressure-electric field" and "pressure-composition". A thermodynamic investigation of the phenomenon permits us to define new characteristic coefficients for this type of depolarization.

Index Headings: Phase transition — Ferro- and antiferro-electricity

Solid solutions suitable for irreversible conversion from mechanical to electric energy take advantage of an hydrostatic-pressure enforced transition from ferroelectric to antiferroelectric ($F \rightarrow AF$).

The diagram in Fig. 1 shows the following transitions for increasing temperature:

- (a) and (c) $AF_A \rightarrow F_B$ } determined from DTA and permittivity plots.
 $AF_A \rightarrow AF_B$ }
 $F_A \rightarrow F_B$ }
 (b) $AF_B \rightarrow F_B$ } (dotted line) determined from hysteresis loops at low frequency [1].
 $AF_A \rightarrow F_A$ }

In the case of x approaching 0.05–0.07 the F and AF states are fairly close at room temperature. It should be born in mind that for all compositions of the perovskite type [2]: the electric field acts to extend the range of stability of the ferroelectric state; and the compressive stress acts to extend the range of stability of the antiferroelectric state.

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In the case of a transition occurring between ferroelectric and antiferroelectric states the most important and most easily noticeable modification is

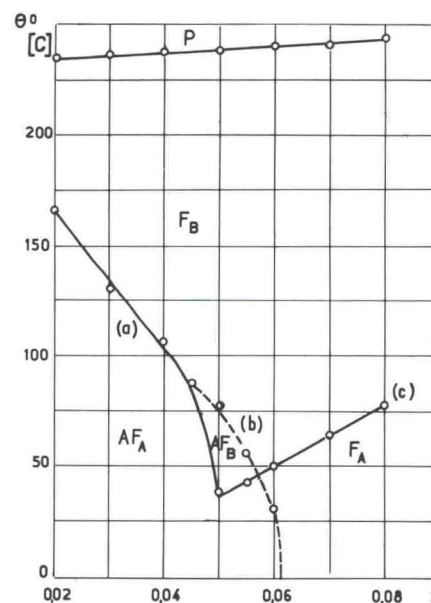


Fig. 1. Temperature-composition phase diagram for $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3 + 0.8\% \text{WO}_3$ with x variable, temperature increasing

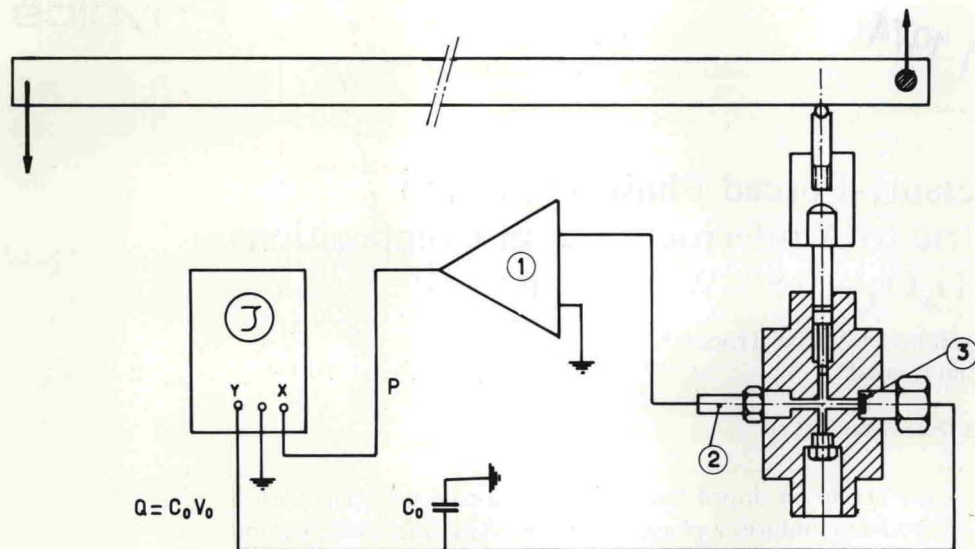


Fig. 2. Schematic diagram of the experimental arrangement, 1 charge amplifier, 2 pressure transducer, 3 ferroelectric ceramic specimen

the loss in remanent polarization of poled specimens [3].

1. Experimental Methods

Experimental Arrangement

Figure 2 exhibits the experimental arrangement used to induce a hydrostatic compression of the ferroelectric ceramics under investigation. The principle of the device is straightforward: a lever arm acts on the primary piston of a high-pressure chamber and allows to reach hydrostatic pressures of the order of 6–7 kbar [4].

Measurements Made on Short-Circuited Specimens (Fig. 3)

A capacitor (1300 μF) is connected to the terminals of the specimen. The Voltage V_0 measured by an oscillograph or a high input-impedance recorder does not exceed a few millivolts. The very high time constant given by the capacitor and the impedance of the measuring apparatus allows either isothermal cycles or "quasi-adiabatic" cycles to be performed within a few hundreds of msec. The cycle is drawn by recording the voltage at the terminals of the capacitance as a function of the pressure. This cycle allows to determine the transition pressure as well as the charges liberated from the ceramic.

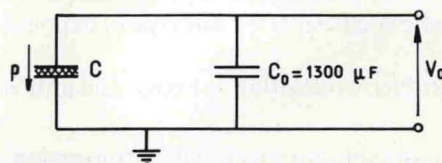


Fig. 3. Measurement circuit

Measurements Made on High Impedance Capacitive Load

A capacitance C_1 of good quality and low value (200 up to 4000 pF) is connected to the terminals of the ceramic. The capacitance C_0 (1300 μF) connected in series within the circuit allows to determine the charge transfers as well as the value of the potential difference at the terminals of the specimen, i.e.

$$V = V_0 \frac{C_0 + C_1}{C_1} \approx V_0 \frac{C_0}{C_1}$$

Preparation of the Specimens

The specimens (diameter: 5 mm, thickness: 1 mm) are covered with a conducting varnish and poled at room temperature under the influence of a 4000 V/mm field. The specimens containing less than 5% titanium are poled when hot (100° C), they cooled under the influence of the field.