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Broadband impedance spectroscopic characterization of $PbTiO_3$ crystal grown by spontaneous crystallization from molten oxides

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Tetragonal lead titanate $PbTiO_3$ single crystals were grown by spontaneous crystallization from a lead and boron oxide flux and investigated by impedance spectroscopy in the broadband frequency range (10^{-3}–5×10^6 Hz) along the crystallographic *a* and *c* axes at room temperature.

Three polarization relaxation modes as well as electric conductivity processes were revealed. In the ultralow frequency range (<10 Hz), the relaxation processes were assigned to the electrode and the ferroelectric domains polarizations. In the high frequency range (10^5 Hz), the relaxation process arises from the crystal lattice polarizations. The electric conduction of the investigated crystals is determined by two fundamental effects – ionic and hopping conductivities. In addition, the anisotropies of relative dielectric constant (300) as well as DC conductivity (1.8×10^{-9} S/m) were estimated.

1. Introduction

Lead titanate ($PbTiO_3$) is a well-known ferroelectric material with a cubic ($Pm\overline{3}m$) – tetragonal *(P4mm)* structural phase transition at around 490 °C [1]. Interest in this class of single crystals is increased significantly during the last decade due its wide use as component of ceramics widely utilized in many applications like the power supplying elements for the wireless sensors [2], high-frequency ultrasonic transducers [3] and pyroelectric applications [4]. Recently, the application of ferroelectric materials in emerging display technologies (e.g. compact laser projection displays for smartphones, active MEMs switcher in AMOLED screens [5]) was suggested. The suitability of these materials for application is governed by their physical properties such as dielectric constant and pyroelectric and piezoelectric properties that, in turn, depend on the type of materials and their methods of fabrication [6].

Currently, $PbTiO_3$ is one of the most used ferroelectric compounds utilized in three different forms: single crystals [7], ceramics [8] and thin films [9]. Lead titanate has a rather high relative constant ($\varepsilon\approx1000$), a low dielectric loss ($\tan(\theta)<1$), which is likely to be influenced by the crystallization process [10]. Furthermore, it was demonstrated that the increase of the dielectric permittivity of $PbTiO_3$ thin films deposited on a crystalline substrate linearly dependents on the annealing temperature [11,12]. In this article we present our results on lead titanate single crystal growth and quantitative characterization of the~~ir~~ dielectric relaxation modes and mechanisms of the electrical of conductivity.

2. Experimental part

2.1. $PbTiO_3$ crystal growth

The flux method was used for $PbTiO_3$ single crystal growth, which comprises universal character and low process temperatures as main advantages. We have previously used it for producing single crystals of materials with high melting point [13–16]. The optimal solvent for lead titanate at 900–1000 °C is a mixture of lead and boron oxides [17]. The latter suppresses evaporation of PbO and thus ensures more stable crystallization of lead titanate in the solution. The charge composition was PbO–86.6 wt%, TiO_2–7.1 wt%, B_2O_3–6.2 wt%. The total weight of the sample was 120 g. Chemically pure grade reagents were used. Single crystals were grown from solutions by spontaneous crystallization in air atmosphere in a 30 mL platinum crucible placed into a resistance

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Fig. 1. Photograph of a single crystal sample of $PbTiO_3$. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

furnace. Temperature control was performed using a PID temperature controller with a type B thermocouple. The crystal growth furnace was described earlier [18]. After all components of the mixture were thoroughly ground in an agate mortar, the flux was heated at 1000 °C for 2 h and then cooled to 925 °C at a rate of 4 K/h. The resulting crystals were separated from the solution residues by boiling in nitric acid. A representative single crystal is presented in the Fig. 1.

The grown crystals had pale yellow color. The chemical composition (Ti – 11.73 ± 0.35 at%, Pb – 12.08 ± 0.36 at%) of the grown crystal was determined with a scanning electron microscope (JeolJSM-7001F) equipped with an energy dispersive X-ray fluorescence spectrometer (Oxford INCAX-max 80). X-ray diffraction analysis of the powdered samples was performed with a Rigaku Ultima IV diffractometer in the 2θ range 10–80° at a scan rate of 1 K/min (Fig. 2). The measured diffraction patterns proved that the grown crystals had a tetragonal lattice with parameters a=3.9015 (4) Å and c=4.1535(5) Å, which is in good accordance with reported data [19]. The peaks at 22°, 27°, 39° shows low content of unknown impurity phase.

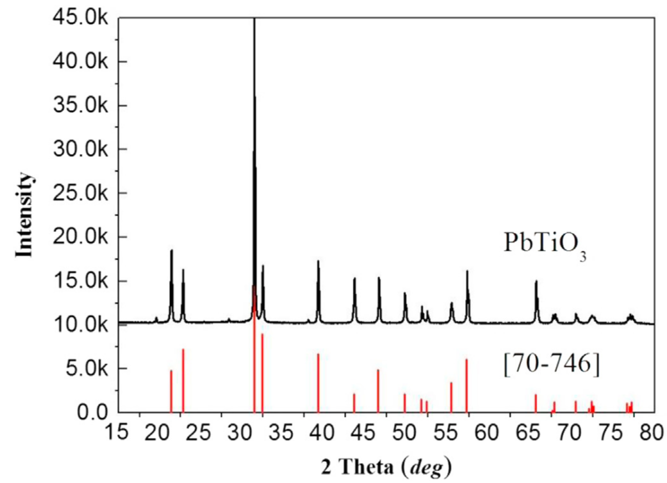

Fig. 2. X-ray diffraction pattern of $PbTiO_3$ and reference data from ICDD [70-746] in the bottom.

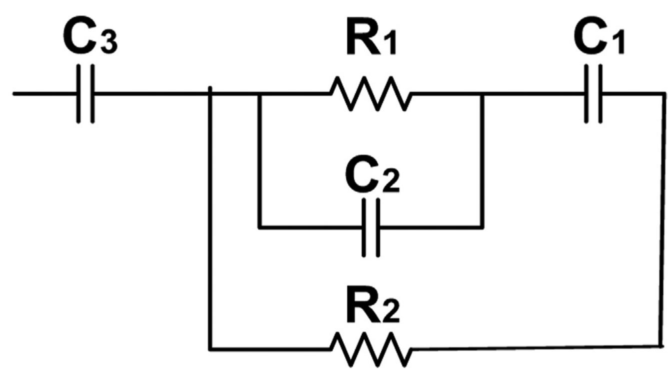

Fig. 3. The equivalent electric circuit of a ferroelectric crystal.

2.2. *Immittance spectroscopic studies of a GROWN $PbTiO_3$ CRYSTAL*

The grown crystal was investigated by an AC impedance spectroscopy technique. This method is a powerful tool for probing electrical properties associated with crystal interiors, grain boundaries and surfaces. This is particularly the case when the results of various methods of data presentations are compared since often, one method alone, such as the use of complex impedance plane plots may give information that is incomplete. With the use of combined impedance, electric modulus and conductivity spectroscopy, it is possible to characterize both bulk phenomena and grain boundary [20–22].

A complex system consisting of a ferroelectric single crystal and electrodes can be described by a simplified equivalent electric circuit shown in Fig. 3. Here the capacitance C_1 describes the contribution to the total polarization associated with the ferroelectric domains. The resistance R_1 describes the losses connected with the re-orientation of the ferroelectric domains. C_2 represents the lattice polarization of the crystal due to atomic displacements of the Pb and Ti ions. R_2 is the leakage resistance of the crystal caused by the long range migration of ions. C_3 is the double-layer capacitance at the crystal-electrode interface.

The real and imaginary parts of the equivalent circuit impedance can be written as