Electromotive Cells in Investigation of Phase Transitions in Ionic Ferroelectric Crystals

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The electrochemical cell: Se|TGSe$_{\text{single crystal}}$|Se, with tri-glycine selenide as solid electrolyte was employed to observe the ferroelectric-paraelectric phase transition. The charge, which normally occurs on the surface of the ferroelectric crystal in the polar phase, is thus incorporated in the electrical double layer of the cell and can be precisely monitored. The pyroelectric currents can also be measured with this cell. The concentration changes on the surface of the single crystal after direct current polarization are observed.

Key words: Ferroelectrics; Phase Transitions.

1. Introduction

The idea of employing electrochemical cells to investigate phase transitions is based on the simple relation of the electromotive force (e. m. f.) to the change of molar free enthalpy for the reaction taking place in the cell. If any of the reactants of the cell reaction undergoes a phase transformation, it should be visible by the dependence of the cell on temperature. This holds for the phase transitions of first order, whereas for second order transitions only an inflection on the e. m. f. dependence is observed. The usual procedure is to prepare the investigated material as electrode material of one of the two electrodes forming the electrochemical cell. When the material used is composed of metals or alloys, there is no difficulty in constructing a suitable electrochemical cell. With this method many phase diagrams of metalic systems were obtained and phase transitions observed [1, 2]. Phase transformations of various alloys were also detected with this method [3]. When the material is a non-conducting organic ferroelectric single crystal like alkylammonium halogenobismutate, it can not be employed as the electrode material; however, the ferroelectric single crystal could be regarded as a low-conducting electrolyte. It is then possible to design electrodes which are reversible for ions present in the lattice of the single crystal. The resulting electrochemical cell includes then the single crystal as the electrolyte, and the transition takes place in the electrolyte material, not in the electrode metallic phase. In case of the ferroelectric-paraelectric phase transition, the electrical charge accumulates at the boundary between electrode and single crystal and adds to the e. m. f. of the cell.

Electrochemical cells with a single ferroelectric crystal as electrolyte were successfully employed for methylammonium chlorobismuthate(III) and bromobismuthate(III) [4]. In those cases one electrode was reversible for bismuth cations and the second silver halide one was reversible for halide ions, e. g.

$$\mathrm{Bi}|(\mathrm{CH_3NH_3})_5\mathrm{Bi_2Cl_{11}}(\text{single crystal})|\mathrm{AgCl, Ag}.$$

This means that for each individual material an adequate cell should be designed.

The electrochemical cell with a single crystal as electrolyte must be measured with an extremely small measuring current (10^{-16} A).

In this paper the advantages of using electrochemical electrodes instead of neutral metallic contact during investigations of the polar properties of ferroelectric single crystals are discussed. The main interest is in the ferroelectric-paraelectric transition in tri-glycine selenide (TGSe).

2. Experimental

The selenium electrodes were made by plating of copper plates with Se by immersion in a dilute solution of selenic acid. The single crystals with different orientations (samples cut perpendicularly to the polar *c*-axis and *b*-direction) of dimensions $5 \cdot 5 \cdot 1.5$ mm^3, polished on silk wetted with glycerine, were placed between electrode plates, and the cell was fixed with an epoxy resin. The cell with electric contacts soldered on the outer sides of the cell was placed in a copper block with a thermistor temperature sensor and immersed in a water jacket vessel connected with the thermostat. Temperature scans were done at a rate of 0.5 deg/min. In each case, the heating-cooling curves were recorded. The e. m. f. values were measured with an accuracy of 0.01 mV and the temperature with ±0.01 deg. The scans were performed using the universal electrochemical meter (EMU, Elektrochema, Wrocław) coupled to a PC. The input resistance was of the order of 10^{16} Ω (10^8 times higher than resistance of the sample). Due to the high electrical resistance of the cell, the measuring set was very sensitive to electromagnetic fields and was carefully shielded. The pyroelectric current was measured as the voltage drop on the 10 MΩ resistor connected in paralell to the cell. The cell was conditioned before temperature scan at 303 K until the e. m. f. reached a constant value. The polarisation of the crystal was performed in the cell by an external direct current (DC) electric field of 300 V at 303 K. Then the cell was cooled below the transition temperature down to 260 K.

3. Results

The electrochemical cell I used in our experiment is represented by the scheme

$$\mathrm{Se}|\mathrm{TGSe}_{\text{single crystal}}|\mathrm{Se}.$$

The measurements were performed on TGSe single crystals of two orientations: parallel and perpendicular to the polar *b*-axis in the temperature range 263–303 K. The results of electromotive force measurements for a perpendicular cut are presented in Figure 1.

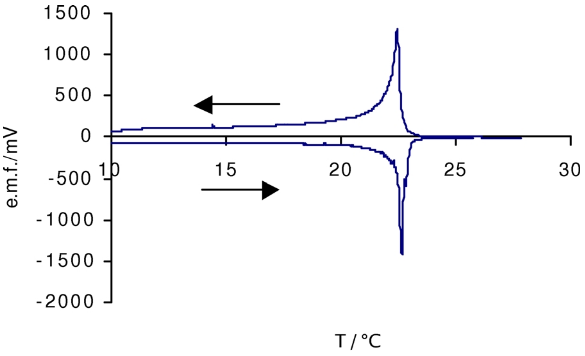

Fig. 1. Results of the e.m.f measurements of cell I versus temperature upon heating and cooling.

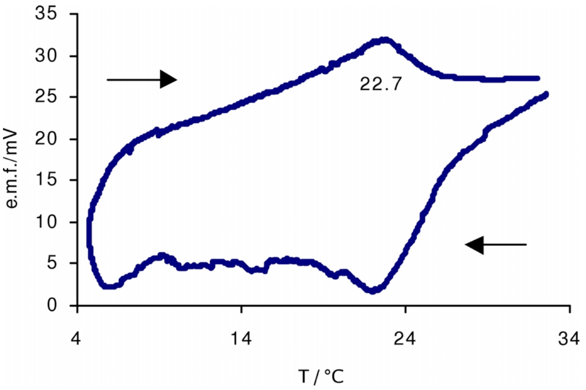

Fig. 2. Results of the e. m. f. measurements of cell I with the paralell cut crystal (the *c*-axis) of TGSe.

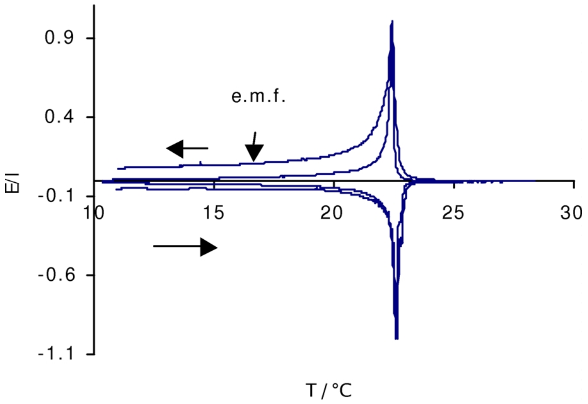

Fig. 3. Normalized scans for the e. m. f. and current of cell I (the outer curve represents the e. m. f., the inner one the current).

Well defined peaks are observed exactly at the transition temperature with a very small temperature hysteresis of 0.2 deg. The paralell cut crystal (the *c*-axis) should not exhibit those peaks, but due to surface roughness and a possible non-exactly parallel construction of the cell, a small effect is observed (Fig. 2).

When the electrochemical cell is shortened with a 10 MΩ resistor, then the potential drop measured on the resistor yields the pyrocurrent for the transition.

The comparison of the shapes of the e. m. f. and pyroelectric currents scans after normalization (actual value divided by the maximal value) are presented in Figure 3.

The differences in the shapes are visible. The advantage of the e. m. f. method is that the measurement with such a low current drain does not influence the

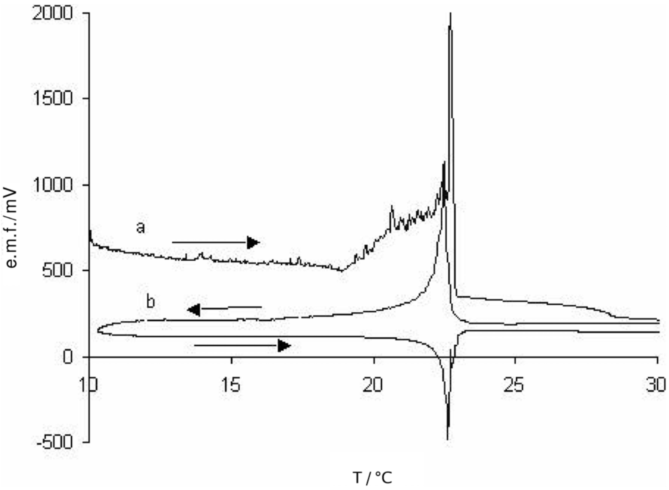

Fig. 4. Cell I after polarization with DC of +300 V (upon heating) (a), compared with the second measurement without DC polarization (b).

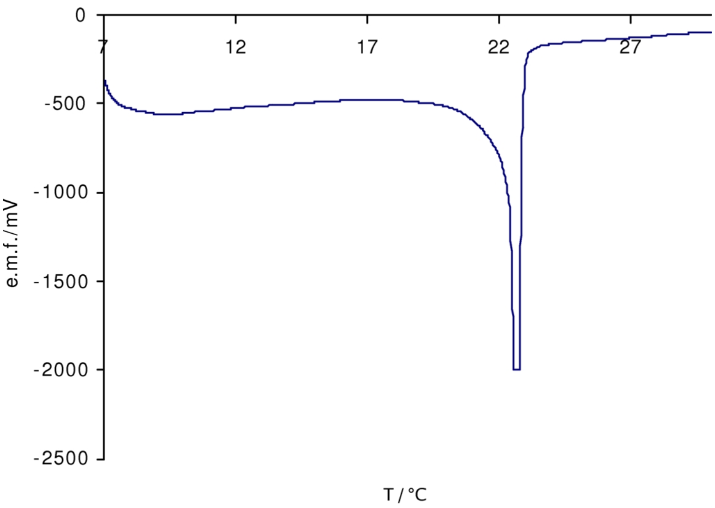

Fig. 5. Cell I after reverse polarization with DC of −300 V (upon heating).

magnitude of the charge on the crystal surface. This is better justified from the thermodynamic point of view.

The polarization of the crystal placed in the cell with an external DC electric field was performed at temperatures higher than the transition temperature. It was intended to induce a monodomain structure of the crystal. However, during DC polarization at elevated temperature, the electrical conductivity of the single crystal increases and the process of electrolysis starts, followed by concentration changes of selenium ions at the boundaries metal-single crystal. The observed e. m. f. after DC polarization changes by several hundred of millivolts, and the e. m. f. for transition is also shifted. When applying a reverse polarization the shift of the potential is also reversed.

Observing the direction of the e. m. f. change during heating, it is visible that the direction of the e. m. f. change induced by applying DC polarization can be in concordance or opposite (as seen on Fig. 4) to the existing initial polarization.

After polarization of the sample, the measurements reveal a characteristic pilling structure on the e. m. f. vs. temperature curve (see Fig. 4).

The reverse polarization yields a negative component of the electrochemical part of the e. m. f., but the charge accumulation on the crystal surface is clearly visible.

For this reversed polarization the pilling structure on the e. m. f.-temperature curve (Fig. 5) is not observed. The temperature dependence of the e. m. f. is of the same character as the dependence of the overpotential

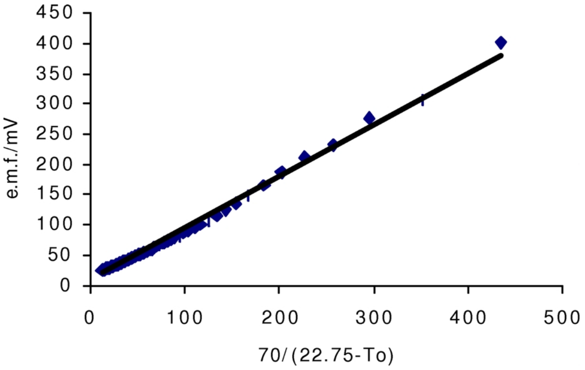

Fig. 6. The e. m. f. dependence, linearized according to the electrocrystalization theory.

observed in the electrocrystallization process of metals which depends on $(T_0 - T)^{-1}$ [5] (Fig. 6), where T_0 is the transition temperature in case of TGSe. It leads to the conclusion that structural changes in the TGSe resembling recrystallization can influence the character of the charge accumulation on the surface of the ferroelectric single crystal.

4. Discussion

The considered single crystals are commonly regarded as dielectric materials, but after a closer look they may be treated as low-conducting electrolytes, enabling the construction of electrochemical cells and measuring the e. m. f. of the cell. The nature of the charge transport in the bulk of the single crystal seems to be of the vacancy type [6]. The concentration polarization, visible after DC polarization, indicates that there is no electronic conduction in the crystal. The temperature dependence of the e. m. f. of a properly designed cell reflects the ferroelectric-paraelectric phase transition phenomena.

The linear plot of the e. m. f. vs. $(T_0 - T)^{-1}$ is in concordance with a general theory of the change of the crystallization overpotential, derived on the basis of chemical potential variation during the change of the size and number of crystal domains [5]. At temperatures below T_0, the number of domains during heating increases by dividing into smaller ones, reaching a maximum at T_0, but during cooling, at this temperature, very fast formation of very small domains starts, which grow in the process resembling crystallization. After DC polarization the process of dividing starts from the monodomain structure.

The change in the total charge observed during heating of the crystal reflects also as the rise of the e. m. f. could be explained by growing of the total surface of all domains, when the domains divide to a greater number of smaller ones. This thermodynamic point of view could be an alternative to the commonly adopted molecular basis of charge generation in ferroelectric crystals. The e. m. f. measurements revealed also that the current flow during the DC polarization experiment causes concentration changes of selenium ions, on the surface of the single crystal, which can be reversed during polarization in the opposite direction. It should be added, that the concentration changes diminish slowly after heating-cooling cycles.

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