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Phase transitions in Ag-based solid electrolytes as detected by thermosonimetry

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Abstract

Observations of the acoustic emission accompanying the solid–solid (polymorphic) phase changes in silver iodide and silver chalcogenides were performed. It has been found that the temperature dependencies of both the number of acoustic events and their counting rate, registered when heating the investigated materials, display distinct anomalies at the temperature corresponding to the polymorphic phase transition occurring in a given substance. The phase transition temperatures determined from the position of these anomalies agree well with the results of control DSC measurements, as well as with the literature data on the temperatures of the transition of investigated materials to the state of superionic conductivity.

Keywords: Thermosonimetry; Polymorphism; DSC; Solid electrolytes

1. Introduction

Acoustic emission (AE) is the phenomenon of generation of transient elastic waves resulting from various internal processes involving the release of elastic energy accumulated in a solid. The primary sources of these waves are local internal displacements in solids (e.g. dislocation movement, formation and propagation of cracks, grain and domain boundaries). These waves propagate from the dynamical source through the material and cause surface displacements detectable by suitable (mainly piezoelectric) transducers [1–3].

A special case of AE is the noises generated in heated or cooled materials [4,5]. This phenomenon is the basis of a new experimental technique for detecting the phase changes and chemical reactions in materials. This technique called thermosonimetry [5] is by definition the registration of the intensity of sound emitted from a substance during the thermal treatment. During the phase changes and chemical reactions the concentration of the primary AE sources rapidly increases, especially when the specific volumes of the parent and daughter phases markedly differ among themselves. This causes an increase of the AE intensity during the phase transitions and chemical reactions and makes the thermosonimetry a very suitable tool for investigations of these processes.

Although Lønvik [5] constructed a prototype for f-ma LINSEIS, the thermosonimeters are not commercially available up to now. The researchers active in the field are using home-made apparatuses (see e.g. [6–9] and references therein).

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The purpose of the present communication is to present a new thermosonimeter built in our laboratory and the results of an attempt to apply the thermosonimetric technique for detection of the solid–solid (polymorphic) phase changes in some inorganic silver salts. Their high-temperature solid phases belong to the class of structurally disordered ionic crystals which are known to be highly conducting solid electrolytes [10–14]. Their electrical conductivity is of the same order of magnitude as that of the best conducting liquid electrolytes and is entirely due to the mobility of silver ions. It is closely related to the high value of the coefficient of diffusion of Ag ions, which is comparable to that in aqueous solutions. In view of this "liquid-like" behaviour of the silver ions, such substances were often described as ionic crystals with "molten cation sublattice" [13].

Superionic conductors (solid electrolytes) are the subject of intensive research activity, spurred by both the science and technology and caused by their unusual properties and a variety of possible practical applications. In many substances, the state of superionic conductivity appears at elevated temperatures and results from a phase transition in given material [11–13]. Therefore, a need arose for new fast, simple and cheap methods to determine the temperatures of the phase transitions leading to the appearance of the superionic conductivity. Elaboration of such techniques would be of great value for studies of new solid electrolytes and other materials by making the determination of phase diagrams of newly obtained products easier, faster and cheaper.

2. Experimental

The block scheme of the thermosonimeter used in the present study is shown in Fig. 1. The apparatus consists of two parts. The first is the detection system. The main part of it is a stethoscope — a glass rod serving as an acoustic wave guide and simultaneously as a sample holder. The bottom end of the stethoscope rests on a piezoelectric transducer, located far away from the heated upper end of the stethoscope. So, the temperature of the transducer equals the room temperature and does not change during heating of the sample. The cavity at the upper end of the stethoscope serves as a container for the investigated sample.

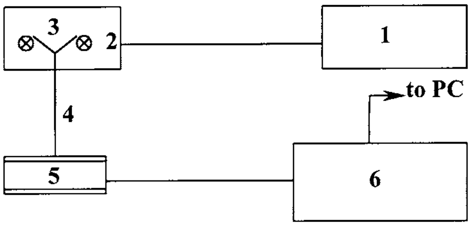

Fig. 1. Block diagram of the thermosonimeter: 1—temperature programmer, 2—optical heating system, 3—measuring chamber, 4—stethoscope, 5—piezoelectric transducer, 6—three-channel acoustic emission analyser.

The sample is heated optically by light from two halogen lamps (each of 50 W), focused on the sample container. The sample temperature is controlled by an iron–constantan thermocouple coupled with a temperature programmer, enabling the sample to be heated at a constant rate of 1, 2, 5, 10, 20, 33 or 50 K/min. The maximum temperature achievable with a linear heating programme is ca. 800 K. The stethoscope and piezoelectric transducer are mounted on the stand with the help of antibouncers. The stand itself is mounted on the heavy steel block with the aid of dampers. This double amortisation system allows for the depreciation of possible artefacts caused by external shocks.

The second part of the thermosonimeter — registration system — is a three channel acoustic emission analyser produced by Institute of Fundamental Problems of Technology of the Polish Academy of Sciences.

The measuring system enables the continuous registration of acoustic events occurring during the programmable heating of the sample. The final product of the measuring procedure are the temperature dependencies of the total number N of the pulses generated by piezoelectric transducer due to acoustic events in the sample and of the intensity of acoustic emission dN/dt.

The control DSC measurements were performed using a NETZSCH differential scanning calorimeter DSC 404/3/F with Pt/PtRh DSC measuring head and platinum sample pans. An empty platinum crucible was used as the reference. The heating rates in the DSC and AE measurements were the same (10 K/min) for each material. All the DSC and AE measurements were performed in atmospheric air under normal pressure.

Table 1
Origin and purity of investigated materials

Compound	Producer	Purity as stated by producer
AgI (silver iodide)	POCh Gliwice	Pure for analyses
Ag_2S (silver sulfide)	Fluka	98%
Ag_2Se (silver selenide)	Aldrich	Reagent grade
Ag_2Te (silver telluride)	Aldrich	Reagent grade

The investigated materials were fine grained powders of silver iodide, silver sulfide, silver selenide and silver telluride. Information about the purity and origin of these materials is given in Table 1.

3. Results and discussion

The experimentally determined temperature dependencies of the AE intensity defined as the counting rate of the acoustic events dN/dT, total number of the acoustic events N counted from the start of the measurement, as well as of the DSC signal for AgI, Ag_2S, Ag_2Se and Ag_2Te are shown in Figs. 2–5.

The temperature dependence of the DSC signal for silver iodide (Fig. 2) displays an endotherm peaking at about 430 K. The deflection point of this endotherm from the base line, located at about 423 K, agrees well with the literature data [12–14] on the temperature of the polymorphic phase transition from the low-conducting hexagonal close packed phase to the superionic body centered cubic phase.

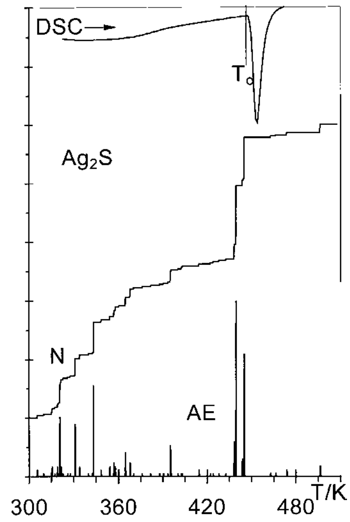

Fig. 3. Temperature dependencies of the AE intensity, total number of acoustic events (N) and DSC signal for silver sulfide.

The position of the DSC endotherm coincides well with the bursts of acoustic events appearing on the

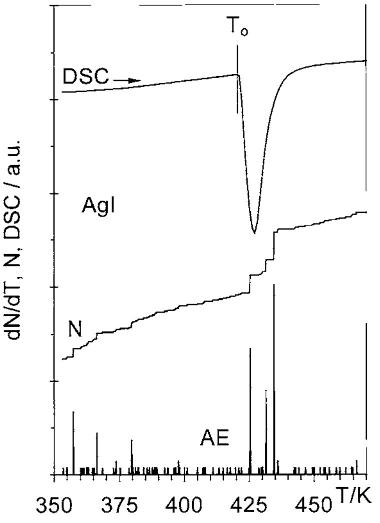

Fig. 2. Temperature dependencies of the AE intensity, total number of acoustic events (N) and DSC signal for silver iodide.

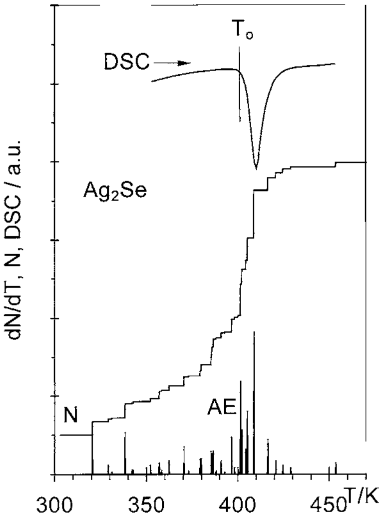

Fig. 4. Temperature dependencies of the AE intensity, total number of acoustic events (N) and DSC signal for silver selenide.

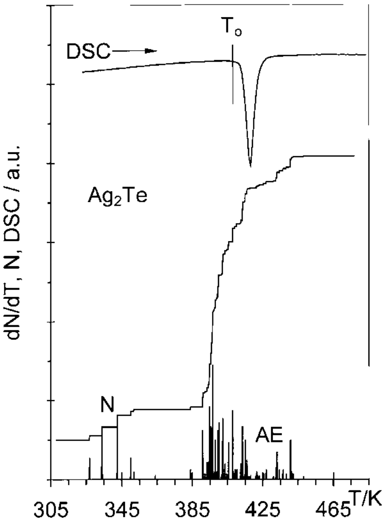

Fig. 5. Temperature dependencies of the AE intensity, total number of acoustic events (N) and DSC signal for silver telluride.

temperature dependence of the counting rate $dN/dT = f(T)$. This increase in the acoustic activity of the sample is also clearly seen on the total number N of acoustic events counted from the start of experiment.

In the case of silver sulfide (Fig. 3) the endotherm on the DSC curve evidences the occurrence of the polymorphic phase change at about 440 K. In the same temperature range a sudden increase in the number of acoustic events is observed and the bursts of the emission intensity (counting rate) occur.

According to the literature data [12–14] silver sulfide transforms at about 440 K from the face centered to the body centered cubic phase. Similarly as the body centered cubic form of silver iodide, the high-temperature phase of silver sulfide is solid electrolyte whose conductivity is entirely connected with the ease of movement of silver cations.

Polymorphic phase transition from the face centered cubic to the body centered cubic phase occurs at about 400 K on heating the silver selenide [12–14]. This is clearly evidenced by an endotherm on the DSC curve with an onset at 400 K and peak at 407 K (Fig. 4). The high-temperature body centered phase of silver selenide is known as a superionic conductor.

In the same temperature interval the burst-like anomalies in the temperature dependence of the counting rate acoustic events are observed. The temperature dependence of the total number of counted acoustic events abruptly increases in the temperature interval of phase transformation.

In contrast to silver iodide, silver sulfide and silver selenide, the high temperature superionic phase of silver telluride is not body centered but face centered cubic [10,11]. It forms on heating the hexagonal form of silver telluride stable at room temperature. The polymorphic phase transition, as evidenced by endotherm on the DSC curve (Fig. 5) starts at about 408 K. In the same temperature interval an enhanced acoustic activity of the sample is observed, as evidenced by the curves representing the temperature dependencies of the counting rate and of the total number of acoustic events counted from the start of experiment.

4. Concluding remarks

The presented results demonstrate the usefulness of the thermosonimetric technique for detection of phase transformations in condensed phase. It seems that further improvement of the apparatus, enabling the registration of the frequency spectrum of acoustic emission accompanying the phase changes, could bring more fundamental information, e.g. about the primary sources of the emission events. It is planned to apply the thermosonimetric technique to control the results of experiments with sonochemical and mechanochemical synthesis of Ag and Cu cations conducting solid electrolytes.

Further works are in progress.

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