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Allotropic transformation of Se_8 to Se_n

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Abstract Single crystals of *cycloocta*-Se, unambiguously characterized by XRD were prepared and used in a study of its allotropic transformation to *polycatena*-Se by DSC supported by Raman spectroscopy and optical microscopy. It was found that the transformation of a Se_8 single crystal to polycrystalline Se_n proceeds progressively within the volume of the monoclinic single crystal without shape change. All the results of DSC, Raman spectroscopy, and optical microscopy indicate that previous proposals on *cycloocta*-Se melting during transformation are not realistic.

Keywords Selenium · Allotropic transformation · Conventional DSC · StepScan DSC · Raman spectroscopy · Optical microscopy

Introduction

Selenium and selenium-based chalcogenide glasses have recently been in the focus of both basic and applied research. This element is well-known to be a very complicated substance; its properties have been studied over years but are still not fully understood in detail, especially due to its great variety of molecular structures. The most stable crystal form is the trigonal selenium (*polycatena*-Se) consisting of helical Se_n chains parallel to the trigonal *c*-axis. Other crystal form is monoclinic selenium (*cycloocta*-Se) based on eight-membered puckered Se rings. Slight structural differences in cyclic arrangement result in existence of four known forms α, β, γ, δ of *cycloocta*-Se [1–5]. The monoclinic form is thermodynamically metastable and spontaneously converts to the trigonal one at higher temperature or slowly after a longer time at ambient temperature. Surprisingly, no newer work on this allotropic transformation has appeared since the original study more than 30 years ago [6].

The final form of solid state selenium is the non-crystalline one (bulk glass or amorphous layer). According to method of preparation, glassy selenium consists of a mixture of chains and rings in various proportions. It was found that both the quenching temperature and the cooling rate during preparation have a crucial influence on the rings/chains ratio, see e.g. [7, 8].

Selenium atoms are covalently bonded irrespective of modification, the chains and/or rings are interconnected to each other by van der Waals forces.

Although selenium and selenium-based glasses have been intensively studied for many years, little attention has been paid to monoclinic selenium, probably because the preparation of this unstable modification, in sufficient quantity, is problematic. In particular, it is necessary to prevent contamination by trigonal selenium. Using more sensitive experimental techniques than were available more than 30 year ago [6], we prepared pure monoclinic selenium and studied its thermally induced allotropic transformation to the trigonal form.

Experimental

Pure monoclinic selenium allotrope was prepared according to [5]. Red irregular hexagonally shaped plate-like single-crystals with diameter up to 200 μm were obtained.

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The crystallographic characterization of Se_8 single-crystal was carried out using a four-circle diffractometer Kappa CCD; Bruker with monochromatized MoK_α radiation ($\lambda = 0.71073$ Å).

Thermoanalytical properties were recorded by power-compensated differential scanning calorimeter Diamond (Perkin-Elmer) using both conventional and StepScan DSC modes. Temperature and enthalpy calibrations of the calorimeter were performed carefully using high purity zinc and indium. The high sensitivity of the calorimeter allows us to work with very small amounts of samples, in our case ca. 1 mg of single-crystals. Samples were crimped in aluminum pans.

Conventional DSC measurements were carried out under the non-isothermal conditions at a heating rate of 10 K/min.

StepScan DSC experiments were carried out with temperature step 1 K, heating rate in the temperature step 20 K/min and isotherm duration either 60 s or with maximal allowed heat flow difference ± 0.1 μW per approx. 2 s before next step.

To obtain the Raman spectrum of pure trigonal crystalline form (Se_n) this form was prepared by long-term heating of a supercooled melt of black selenium in an evacuated quartz ampoule at 190 °C, which is relatively close to the melting point of trigonal crystals ($T_{ons} =$ 219 °C), and its structure was verified by XRD.

Raman spectra of the Se_8 single crystal, polycrystalline Se_n and a temperature dependent set of spectra completely covering the temperature region of allotropic transformation (50–140 °C) were measured using an Eclipse E400 microscope (Nikon), with THMS 600 stage, coupled to Raman module FRA 106 of FTIR spectrometer IFS 55 (Bruker) with Nd:YAG excitation laser (1064 nm) and Ge-detector cooled by liquid nitrogen.

Visually observable temperature dependent changes of Se_8 single crystals were studied using optical microscope BX 60 (Olympus) equipped with a heating stage THMS 600 (Linkam) for high temperature measurement.

The Solo + MIA chemometrics program package (Eigenvector Research Inc., Wenatchee, Washington, USA) was used for analysis of dependency of spectra on temperature.

Results and discussion

Fresh single crystals of monoclinic selenium must have been prepared immediately before experiments because of their instability. Slow allotropic transformation is observable after a few days even at room temperature.

XRD analysis was employed to confirm that pure single-crystals of monoclinic δ-Se_8 allotrope were prepared, see [5] for detailed crystallography. This ensures that no other selenium allotropes (in particular no trigonal selenium) as well as no glassy phase were used in this study.

Thermally induced allotropic transformation of δ-Se_8 single crystals to Se_n was studied by differential scanning calorimetry. Two subsequent heating scans are shown in Fig. 1. During the first scan, an endothermic process with a maximum at 103 °C and enthalpy change $+5$ J g^{-1} starts at $\sim$74 °C. This process directly turned to exothermic processes (overall enthalpy -30 J g^{-1}) with one shoulder at approx. 118 °C and two well-resolved maxima at 123 and 134 °C. The subsequent endotherm with onset at 219 °C and enthalpy $+77.9$ J g^{-1} can be clearly recognized as the melting of trigonal selenium (*polycatena*-Se; Se_n). The formation of trigonal selenium was confirmed by both XRD and Raman spectroscopy.

The subsequent DSC scan (2nd scan) shows at first a glass transition at 41 °C, as expected after cooling of Se_n melt, followed by only one exothermic change with a maximum at $\sim$140 °C. That change corresponds unambiguously to the crystallization of Se_n supercooled liquid. Finally, melting of trigonal selenium was again observed, see Fig. 1. It is evident that the endothermic process observed during the first scan above 75 °C comprises the first step of the irreversible transformation of selenium allotrope.

To minimize the influence of heating on transformation kinetics, we used a quasi-isothermal DSC technique (StepScan DSC). The result obtained differs significantly from that obtained by conventional DSC. The kinetic part of StepScan DSC revealed that a quasi-isothermal transformation starts almost at the same temperature as that upon heating (conventional DSC); however, the transformation process is entirely exothermic, see Fig. 2. Quasi-isothermal

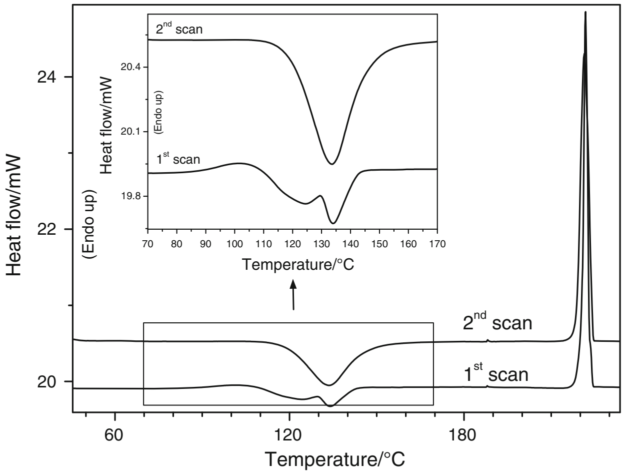

Fig. 1 Heating scans of monoclinic selenium (Se_8); conventional DSC, $q = 10$ K/min. For details, see text

transformation starts with a rather small but well-resolved isolated exotherm (approx. -0.5 J g^{-1}) followed immediately by broad three peaked shape exotherm of overall enthalpy change -26 J g^{-1} from 84 to 129 °C. The isobaric specific heat capacity (measured by StepScan DSC, reversible part) changes in course of allotropic transformation only slightly from approx. 0.58 J $g^{-1}K^{-1}$ up to 0.59 J $g^{-1}K^{-1}$, across a minimum 0.53 J $g^{-1}K^{-1}$ at 117 °C.

To reach a decision about the origin of the complicated shape of the transformation exotherms (DSC, StepScan DSC) temperature dependent Raman spectroscopy was used. Typical spectral shape changes can be seen in Fig. 3 and the spectra of both pure Se_8 and Se_n crystals at room temperature in Fig. 4. The set of temperature dependent Raman spectra was analysed by Multivariate Curve Resolution analysis (MCR). Two pure components (Fig. 5), and the temperature dependence of their contributions were resolved, Fig. 6. Comparing resolved components with Raman spectra of pure crystalline selenium allotropes one can clearly observe that *cycloocta*-Se transforms progressively to *polycatena*-Se in the temperature region 80–130 °C without any other phase change, such as crystal melting and subsequent crystallization [6]. This temperature region overlaps perfectly with the transformation region observed in StepScan DSC, see Fig. 6.

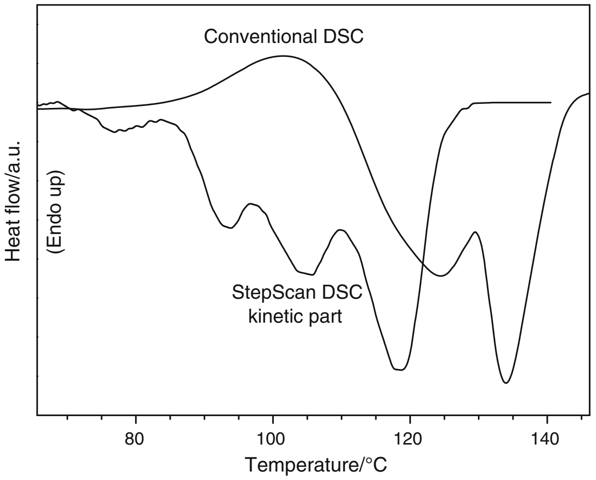

Fig. 2 Non-isothermal (conventional DSC) and quasi-isothermal (StepScan DSC) measurements of the selenium allotropic transformation

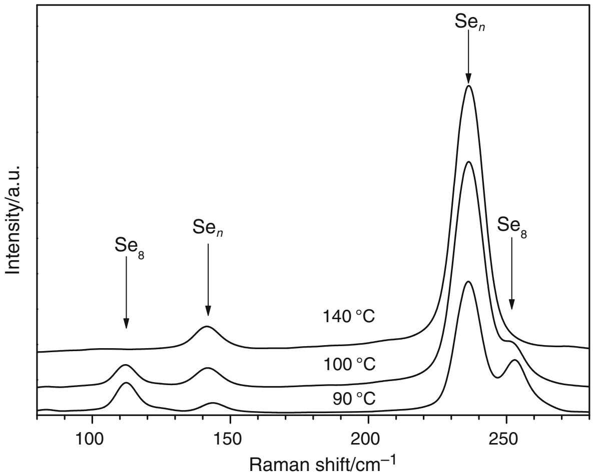

Fig. 3 Raman spectra measured in the course of the selenium allotropic transformation

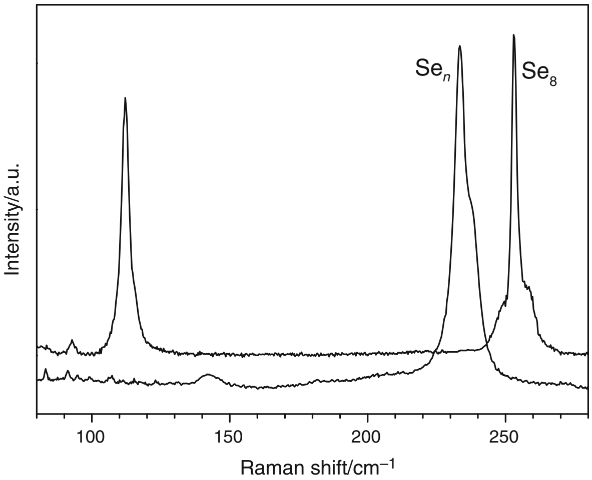

Fig. 4 Micro-Raman spectra of Se_8 single crystal and polycrystalline Se_n

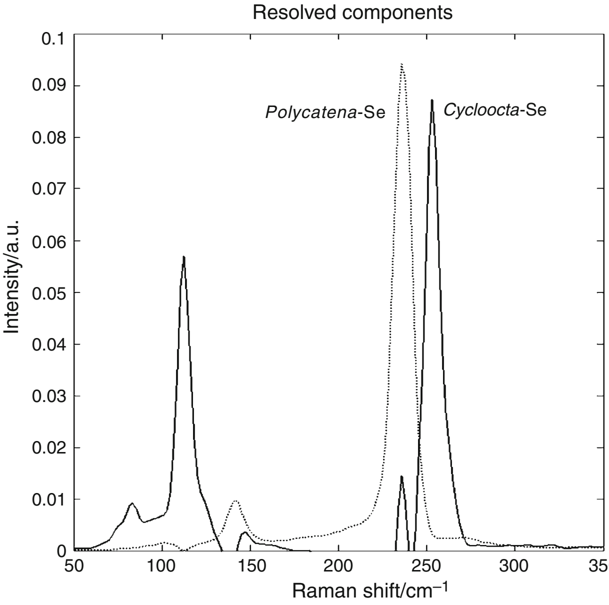

Fig. 5 Pure components resolved by MCR analysis from the set of Raman spectra of allotropic transformation

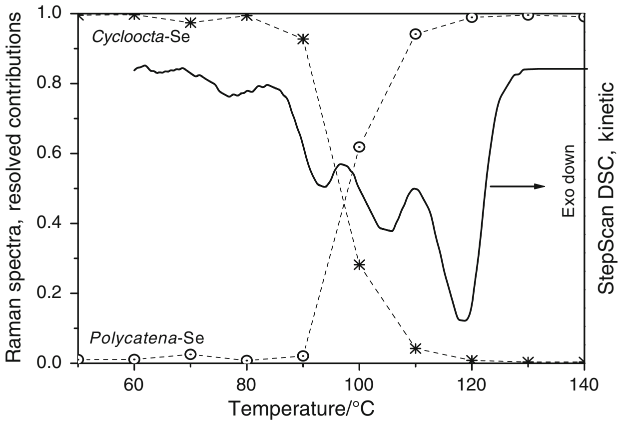

Fig. 6 Resolved contributions of pure components (see Fig. 5) compared with quasi-isothermal kinetic part of StepScan DSC

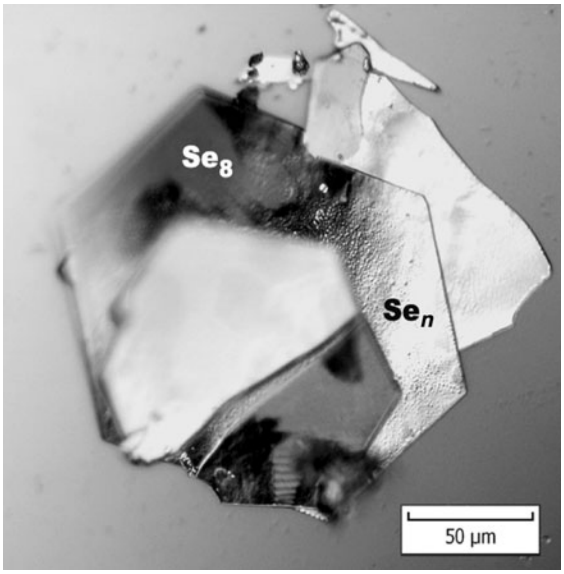

Fig. 7 Microphotography (in reflected light) of Se_8 single crystal partially transformed onto Se_n. Transparent part of Se_8 single crystal can be resolved well from the opaque one constituted by polycrystalline Se_n. Original single crystal shape has not changed

Optical microscopy confirms that allotropic transformation proceeds gradually in the volume of *cycloocta*-Se single-crystal changing this into polycrystalline *polycatena*-Se without changing the original single-crystal shape, Fig. 7.

Apart from the conclusion that crystal melting is *not* a step of allotropic transformation, we must stress that the missing endotherm on the StepScan DSC kinetic curve is curious because bond breaking (ring opening) must be one of the steps of the transformation. To explain this experimental result, we propose that bond breaking is the slowest process, and thus the experimental time plays a crucial role when attempting to observe the related endotherm. Ring opening is spread over a wide temperature interval in quasi-isothermal mode and, as a consequence, the bond breaking endotherm is difficult to observe experimentally. This is not a case of conventional DSC where the markedly shorter experimental time shifts slow kinetic effect up to higher temperatures and because of higher transformation rate (and therefore a shorter transformation time) endotherm becomes observable. Generally, differences between the experimental and. the relaxation time are the reason for the shift in kinetic effects to higher temperatures when conventional DSC is used, cf. Fig. 2.

Unfortunately, the origin of the complicated shape of both, conventional DSC and StepScan DSC exotherms still remains unclear. As *cycloocta*-Se single-crystal melting can be excluded, we can associate the three-peaked shape of the DSC exotherm with still unidentified complex allotropic transformation mechanism.

Conclusions

Freshly prepared single crystals of monoclinic selenium were used for study of its allotropic transformation to trigonal form. Using both conventional and StepScan DSCs, it was found that allotropic transformation is irreversible kinetic process reaching experimentally observable transformation rate at approx. 80 °C. DSC results combined with Raman spectroscopy and optical microscopy showed that allotropic transformation takes place progressively in the solid state without the melting previously assumed. DSC techniques showed that transformation proceeds in three and/or four steps. We can conclude that irreversible allotropic transformation of monoclinic selenium is mainly a kinetic process proceeding without melting but, unfortunately, the mechanism of individual transformation steps is still not completely clear.

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