

STUDYING Cu_{2-x}Se PHASE TRANSFORMATION THROUGH DSC EXAMINATION

*K. Chrissafis**, *K. M. Paraskevopoulos* and *C. Manolikas*

Physics Department, Aristotle University of Thessaloniki, 54124, Thessaloniki, Greece

The thermal effect accompanying the transition of Cu_{2-x}Se into a superionic conduction state was studied by non-isothermal measurements, at different heating and cooling rates ($\beta=1, 2.5, 5, 10$ and $20^\circ\text{C min}^{-1}$). During heating the peak temperature (T_p) remains almost stable for all values of β , ($136.8\pm 0.4^\circ\text{C}$ for Cu_2Se and $133.0\pm 0.3^\circ\text{C}$ for $\text{Cu}_{1.99}\text{Se}$). A gradual shift of the initiation of the transformation towards lower temperatures is observed, as the heating rate increases. During cooling there is a significant shift in the position of the peak maximum (T_p) towards lower temperatures with the increase of the cooling rate. A small hysteresis is observed, which increases with the increase of the cooling rate, β . The mean value of transformation enthalpy was found to be $30.3\pm 0.8 \text{ J g}^{-1}$ for Cu_2Se and $28.9\pm 0.9 \text{ J g}^{-1}$ for $\text{Cu}_{1.99}\text{Se}$. The transformation can be described kinetically by the model $f(\alpha)=(1-\alpha)^{n(1+k_{\text{cat}}x)}$, with activation energy $E=175 \text{ kJ mol}^{-1}$, exponent value n equal to 0.2, $\log A=20$ and $\log(k_{\text{cat}})=0.5$.

Keywords: chalcogenides, crystal growth, differential scanning calorimetry (DSC), phase transactions

Introduction

During the last decade, a variety of superionic conductors have received attention from a technological and physical point of view. Copper chalcogenides are considered as promising in electronic technology due to their interesting physicochemical properties [1, 2 and references therein]. Copper selenide belongs to this family; it presents a series of members with a wide range of stoichiometric deviations as expressed by the formula Cu_{2-x}Se and shows mixed conduction [3]. In the high temperature superionic phase, this compound has an FCC structure. However, there are small variations in the proposed structure of the β phase in the existing literature [4–6]. According to Heyding's phase diagram [7], its high temperature phase (the phase with superionic properties) exists over a wide range of temperatures and compositions. The superionic $\beta\rightarrow\alpha$ transition temperature is $\sim 141^\circ\text{C}$ for Cu_2Se and decreases with increasing deviation from stoichiometry [8]. At this temperature the transition is discontinuous and corresponds to an order-disorder transition. For nonstoichiometric samples (Cu_{2-x}Se) there is a change in the nature of the transition of the samples, from polymorphic $\beta\rightarrow\alpha$ (when $x<0.1$) to eutectoid ($\beta\rightarrow\alpha+\text{Cu}_2\text{Se}_3$), which takes place when $x>0.1$ [9]. For samples with $x<0.02$, there are two different experimental results and interpretations about the nature of the transition into the superionic conduction state. According to the first, two close phase transitions were observed below

140°C [10]. The lower-temperature transition is a second order, with an order-disorder character. The higher transition remains discontinuous, of first order, which is essentially an order-disorder transition in the b direction. According to the second, no signs of branching in the phase transition were observed when x increased from 0.0 to 0.05 [8].

The transformation has been followed experimentally using DTA and has been described in general, but a complete study is absent from the literature. In this paper we study the nature of the transformation with non-isothermal measurements at different heating and cooling rates. Also, we present the thermal behavior of samples with very slight divergence from stoichiometry, and the results are compared with the ones from samples of Cu_2Se .

Experimental

The compounds were prepared by mixing the appropriate quantities of Cu and Se in a quartz tube, sealed under vacuum. The ingot was melted by heating at 1180°C , held at that temperature for 24 h, and then cooled slowly through the melting point (1115°C) and faster down to room temperature. The material obtained was sliced and the composition and homogeneity of the slices were checked by SEM-EDS analysis.

The thermal behavior of Cu_2Se and Cu_{2-x}Se ($x=0.01$) was studied using a Setaram DSC 141 calorimeter. The temperature and energy calibrations of

* Author for correspondence: hrisafis@physics.auth.gr

the instrument were performed using the well-known melting temperatures and melting enthalpies of high purity standards, i.e. In, Sn and Zn. The Cu_2Se and $\text{Cu}_{1.99}\text{Se}$ bulk samples, about 22 mg in mass, were thermally treated using aluminum crucibles under a constant nitrogen flow. All the DSC measurements were non-isothermal and consisted of complete thermal cycles (heating and cooling) with the same heating/cooling rate (β). The rates varied from 1 to $20^\circ\text{C min}^{-1}$. The same sample was used for all the heating-cooling cycles. However, in order to test the reproducibility of the results, the whole set of measurements was carried out on different samples.

Results and discussion

A complete thermal cycle (heating-cooling) of the phase transformation of a typical Cu_2Se sample, obtained at a rate $\beta=1^\circ\text{C min}^{-1}$ is given in Fig. 1. The hysteresis, the difference between the temperatures of the endothermic peak – during heating – and the exothermic peak – during cooling –, is $\Delta T=2.3^\circ\text{C}$, for heating and cooling rate $\beta=1^\circ\text{C min}^{-1}$. In Fig. 2 the

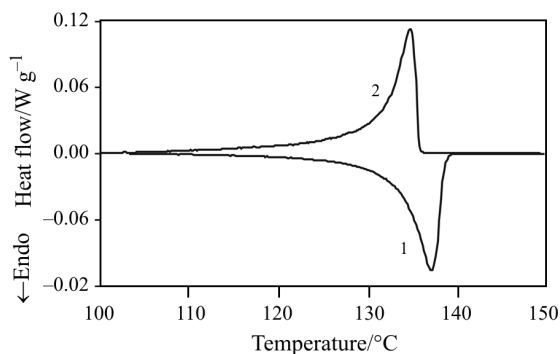


Fig. 1 Thermoanalytical curves of Cu_2Se on heating and cooling with rate $\beta=1^\circ\text{C min}^{-1}$. 1 – heating, 2 – cooling

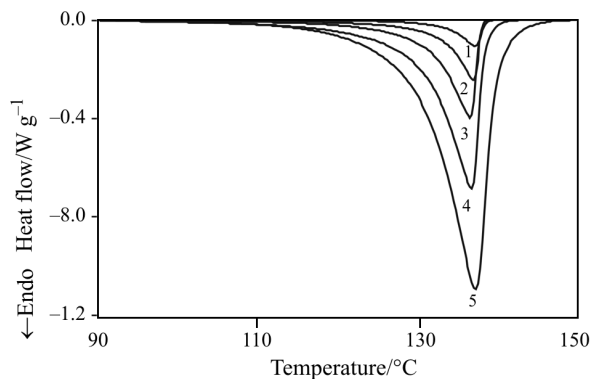


Fig. 2 The influence of the heating rate β on the thermoanalytical curves of Cu_2Se . 1 – 1°C min^{-1} , 2 – $2.5^\circ\text{C min}^{-1}$, 3 – 5°C min^{-1} , 4 – $10^\circ\text{C min}^{-1}$, 5 – $20^\circ\text{C min}^{-1}$

DSC curves (endotherms) obtained at different heating rates ($\beta=1, 2.5, 5, 10$ and $20^\circ\text{C min}^{-1}$) are shown. For these values of β , the peak temperature (T_p) remains almost stable ($136.8\pm 0.4^\circ\text{C}$). On the other side, a gradual shift of the initiation of the transformation towards lower temperatures is observed, as the heating rate increases. The transformation enthalpy was evaluated from the area below the endotherm for each heating rate and its mean value was found to be $30.3\pm 0.8 \text{ J g}^{-1}$.

In Fig. 3 the DSC curves (exotherms) of the Cu_2Se samples taken during cooling at two different cooling rates ($\beta=1$ and $2.5^\circ\text{C min}^{-1}$) are shown. There is a remarkable shift in the position of the peak maximum (T_p) towards lower temperatures with the increase of the cooling rate. The observed hysteresis is present in all cycles taken at different rates and its value increases with the increase of the rate β .

In Figs 4 and 5 the influence of different heating and cooling rates on the thermal behavior of a typical sample of Cu_{2-x}Se ($x=0.01$) is presented. The peak temperature (T_p) during heating remains almost stable ($133.0\pm 0.3^\circ\text{C}$). The mean value of the transformation

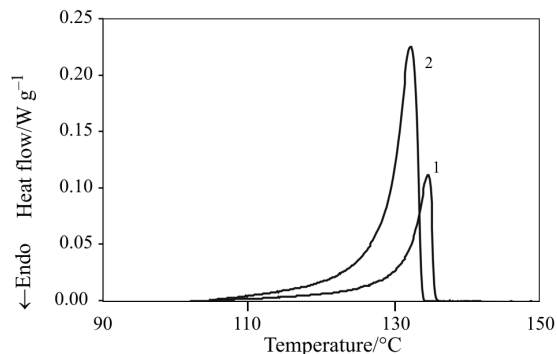


Fig. 3 Thermoanalytical curves recorded at different cooling rates. 1 – 1°C min^{-1} , 2 – $2.5^\circ\text{C min}^{-1}$

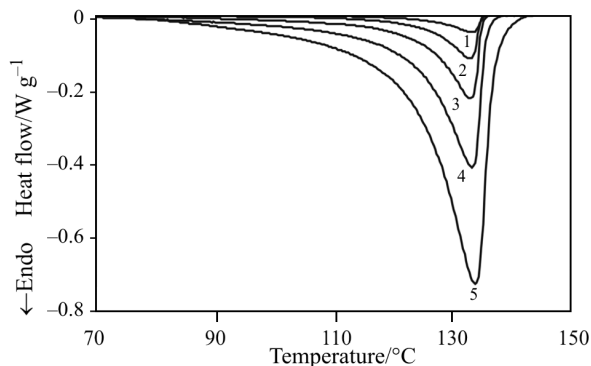


Fig. 4 The influence of the heating rate β on the thermoanalytical curves of $\text{Cu}_{1.99}\text{Se}$. 1 – 1°C min^{-1} , 2 – $2.5^\circ\text{C min}^{-1}$, 3 – 5°C min^{-1} , 4 – $10^\circ\text{C min}^{-1}$, 5 – $20^\circ\text{C min}^{-1}$

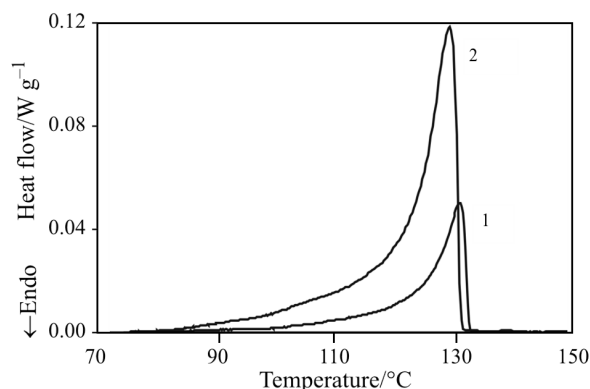


Fig. 5 Thermoanalytical curves recorded at different cooling rates. 1 – 1°C min^{-1} , 2 – $2.5^\circ\text{C min}^{-1}$

enthalpy is found $28.9 \pm 0.9 \text{ J g}^{-1}$. The hysteresis, for a cooling rate of 1°C min^{-1} , $\Delta T = 1.9^\circ\text{C}$ at T_p and it is smaller than that for Cu_2Se .

Taking into account the results shown in Figs 3 and 5, we can conclude that there may be a connection between the hysteresis of the transformation and the different heating and cooling rates. Two sets of experiments were conducted to investigate this connection. In the first set, the samples were heated at the same heating rate ($10^\circ\text{C min}^{-1}$), while different cooling rates (1 and $2.5^\circ\text{C min}^{-1}$) were used. The hysteresis found was the same as that shown in Figs 3 and 5. In the second set of experiments we used two different heating rates (5 and $10^\circ\text{C min}^{-1}$) and we kept stable the cooling rate $2.5^\circ\text{C min}^{-1}$. The two cooling curves coincided. From these experiments we can conclude that the hysteresis depends only on the cooling rate and not on the heating rate.

As can be observed in Figs 2 and 4, the endotherms present considerable asymmetry. The transformation seems to begin gradually, especially far from the peak temperature, while it is completed relatively fast. Exactly the opposite is observed during the cooling process (Figs 3 and 5). In Fig. 6, the thermoanalytical curves of both materials are compared dur-

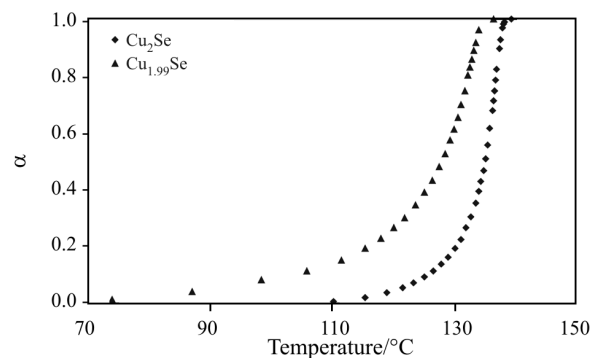


Fig. 6 T/α curves of Cu_2Se and $\text{Cu}_{1.99}\text{Se}$ on heating and cooling with rate $\beta = 1^\circ\text{C min}^{-1}$

ing their heating at a rate of 1°C min^{-1} in the T vs. α form, α being the fractional extent of the transformation at each temperature. The difference that can be noticed is that for $\text{Cu}_{1.99}\text{Se}$, the initiation of the transformation shifts much more towards lower temperatures than for Cu_2Se . It is characteristic that for Cu_2Se the first 10% of the transformation is completed over 15°C , while for $\text{Cu}_{1.99}\text{Se}$, almost the double temperature range is required, 28°C , for the transformation of the same percentage. From the experimental data presented above, it is shown that the behavior of both materials is similar. The temperature of the transformation in $\text{Cu}_{1.99}\text{Se}$ has been decreased, this being in accordance with the literature [9].

According to Ubbelohde [11] and Rao *et al.* [12] the thermal hysteresis may be attributed to the formation of a hybrid phase in a narrow temperature range around the transition temperature. It consists of a mixture of the two phases, as it has already been followed in Cu_2Se transition state, by electron diffraction patterns [4]. Due to the volume change of the monoclinic unit cell with respect to the cubic one, the coexistence of the two phases causes the formation of considerably strong strains inside the material. The corresponding energy, which is stored in the hybrid phase, is the main factor controlling the hysteresis. The increase of the hysteresis, on the other hand, with an increasing cooling rate, may be attributed to kinetic barriers, which the nucleation barriers must overcome in order for the nucleation of the β -phase to start [12].

For the identification of the mechanism of the transformation we carried out a kinetic. A general expression for the transformation rate of a simple process is [13, 14]

$$\beta \frac{d\alpha}{dT} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (1)$$

where α is the fractional extent of conversion at time t , $f(\alpha)$ is the conversion function, a function of α depending on the transformation mechanism, A the pre-exponential factor, E the activation energy, β the heating rate and T is the absolute temperature.

According to the experimental data, during heating, the temperatures of the onset and the endothermic peak remain almost constant for all the different heating rates. It is not observed a shift in the onset and the endothermic peak towards higher temperatures, with the increase in the heating rate. Consequently, methods that require experimental data corresponding to different heating rates (isoconversional methods) and a shift in the experimental peak temperature with the increase of the heating rate, can not be used. The method that has been applied to all data, and the different heating rates separately, is referred as the 'model-free method' [15–17]. It has been character-

ized ‘model-free method’ as according to this approach, no model is applied and it is not necessary for the fitting the knowledge of anyone of the three unknown parameters: the conversion function, $f(\alpha)$, the activation energy E and the pre-exponential factor A . For the fitting of the experimental measurements (heat flow and temperature), a software specially designed for kinetics of thermal analysis is used.

Single heating rate methods, although can give reasonable kinetic triplets $[E, f(\alpha), A]$, are useless in specific cases such as the case where the actual reaction model differs from the assumed one and the case of a multi-step reaction. For this reason we have applied this model to the data sets of all different heating rates.

The form of the curves is particularly asymmetric and it is relatively small the temperature area that corresponds to the fractional extent of the transformation $0.3 < \alpha < 1$ [5.4°C for the rate 1°C min^{-1} , while for $0 < \alpha < 0.3$ it is 22.5°C]. Due to the lack of additional data in the literature related to the transformation at the first fractional extent – more from one transformation at the same time, the one being of second order – we proceeded in the identification of the transformation mechanism taking into account in the fitting procedure, that the transformation during heating is described by one equation $f(\alpha)$. Sixteen different equations (power law, nucleation and growth, diffusion, phase-boundary reaction and n -order reactions kinetic models) were used for the fitting of $f(\alpha)$.

In Fig. 7 are shown, as an example, the results for $\beta = 5^\circ\text{C min}^{-1}$ for Cu_2Se . In this case the form of the conversion function obtained by fitting is $f(\alpha) = (1 - \alpha)^{n(1+k_{\text{cat}}x)}$, with activation energy $E = 175 \text{ kJ mol}^{-1}$, exponent value n equal to 0.2, $\log A = 20$ and $\log(k_{\text{cat}}) = 0.5$. This model is characterised as n th-order reaction with autocatalysis through the reactants X (X is a product in the complex model). This equation was originally formulated on the concept of ‘nucleus branching’, analogous to homogenous chain reactions [13]. The type of conversion function that

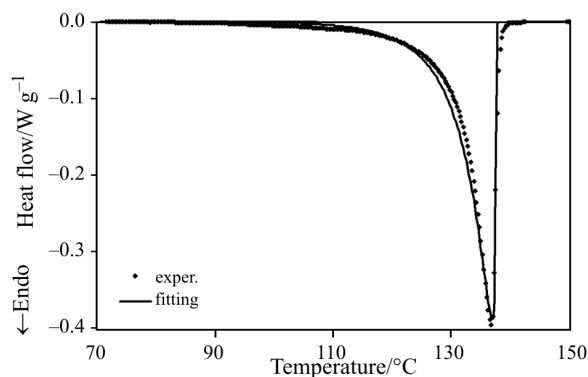


Fig. 7 Fitting of the experimental results, sample Cu_2Se on heating with rate $\beta = 5^\circ\text{C min}^{-1}$

fits the experimental data is the same for all heating rates. The fitting results regarding the values of E and the other parameters are of the same order of magnitude for all the heating rates ($E = 175 \pm 9 \text{ kJ/mol}$, $n = 0.2 \pm 0.02$, $\log A = 20 \pm 1.5$ and $\log(k_{\text{cat}}) = 0.5 \pm 0.05$). For all the other types of conversion function, the deviation in the calculation of the parameters (E , A) is higher, the correlation coefficient of the fitting procedure being remarkably lower.

Of course, the adoption of the particular model for the $f(\alpha)$ cannot be absolute due to the fact that the experimental data do not give further indication of the nature of the transformation in the initial phase. The application of the method and the model succeeded in the description of the primary, particularly expanded temperature area of the transformation, as the other ones concern more symmetrical forms of endothermic curves.

Conclusions

The behavior of the two comparatively examined materials is similar. The phase transformation occurs at a peak temperature $136.8 \pm 0.4^\circ\text{C}$ for Cu_2Se and $133.3 \pm 0.3^\circ\text{C}$ for $\text{Cu}_{1.99}\text{Se}$. It is followed by a small hysteresis between heating and cooling, which increases with an increase of the cooling rate, β . In $\text{Cu}_{1.99}\text{Se}$ the hysteresis is slightly smaller than that in Cu_2Se . During heating the temperature of the endothermic peak remains almost constant for all the different heating rates. The transformation can be described kinetically by the model "nth-order reaction with autocatalysis by X " $f(\alpha) = (1 - \alpha)^{n(1+k_{\text{cat}}x)}$, with activation energy $E = 175 \text{ kJ mol}^{-1}$, exponent value n equal to 0.2, $\log A = 20$ and $\log(k_{\text{cat}}) = 0.5$.

References

- 1 Y. Xie, X. Zheng, X. Jiang, J. Lu and L. Zhu, *Inorg. Chem.*, 41 (2002) 387.
- 2 Y. Jiang, B. Xie, J. Wu, S. Yuan, Y. Wu, H. Huang and Y. Qian, *J. Solid State Chem.*, 167 (2002) 28.
- 3 T. Ishikawa and S. Miyatani, *Phys. Soc. Japan*, 42 (1977) 159.
- 4 N. Frangis, C. Manolikas and S. Amelinckx, *Phys. Status Solidi. A*, 126 (1991) 9.
- 5 O. Milat, Z. Vucic and B. Ruscic, *Solid State Ionics*, 23 (1987) 37.
- 6 S. Kashida and J. Akai, *J. Phys. C*, 21 (1988) 5329.
- 7 R. D. Heyding, *Can. J. Chem.*, 44 (1966) 1233.
- 8 S. A. Danilkin, A. N. Skomorokhov, A. Hoser, H. Fuess, V. Rajevac and N. N. Bickulova, *J. Alloys Comp.*, 361 (2003) 57.
- 9 N. Kh. Abrikosov, V. F. Bankina, M. A. Korzhuev, G. K. Demenskii and O. A. Teplov, *Sov. Phys. Solid State*, 25 (1983) 1678.

- 10 Z. Vucic, O. Milat, V. Horvatic and Z. Ogorelec, *Phys. Rev. B*, 24 (1981) 5398.
- 11 A. R. Ubbelohde in 'Reactivity of Solids' Ed., J. H. de Boer (1961).
- 12 K. J. Rao and N. R. Rao, *J. Mater. Sci.*, 1 (1966) 238.
- 13 A. K. Galwey and M. E. Brown in: *Handbook of Thermal Analysis and Calorimetry*, Elsevier, Amsterdam, 1998.
- 14 M. E. Brown, M. Maciejewski and S. Vyazovkin, *Thermochim. Acta*, 355 (2000) 125.
- 15 S. Vyazovkin and C. Wight, *Thermochim. Acta*, 340-341 (1999) 53.
- 16 H. Polli, L. A. Pontes and A. S. Araujo, *J. Therm. Anal. Cal.*, 79 (2005) 383.
- 17 P. Simon, *J. Therm. Anal. Cal.*, 82 (2005) 651.

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