**UDC 544.31:546.56'661.693/23**

# CALORIMETRIC STUDY OF PHASE TRANSITION OF $Cu_8GeSe_6$ AND COMPARISON WITH OTHER ARGYRODITE FAMILY COMPOUNDS

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*Received 02.10.2023*
*Accepted 23.10.2023*

***Abstract:*** *This work is a continuation of our work on the thermodynamic study of synthetic analogues of the mineral argyrodite. In this work, a calorimetric study of the phase transition of the Cu8GeSe6 compound was carried out using the differential scanning calorimetry (DSC) method. Based on the data of DSC curves of samples of the studied compound with different masses, the temperature and enthalpy of the phase transition from the low-temperature orthorhombic modification to the high-temperature cubic modification were established. Using the Gibbs-Helmholtz equation, the entropy of the phase transition was also calculated and the comparative analysis of the obtained thermodynamic values of the studied compound with other argyrodite phases was carried out.*

***Keywords:*** *phase transition, thermodunamic functions, copper-germanium selenide, differential scanning calorimetry.*
***DOI: 10.32737/2221-8688-2023-4-396-403***

## Introduction

The mineral argyrodite ($Ag_8GeS_6$) was the first representative of a large family of compounds which is nowadays called argyrodites. These phases have the general formula $A^{m+}_{(12-n)/m}B^{n+}X^{2-}_6$, where m and n are the valences of cations A and B, respectively. Here, A-cations may be $Cu^+$, $Ag^+$, $Cd^{2+}$, $Hg^{2+}$; B-cations are $Ga^{3+}$, $Si^{4+}$, $Ge^{4+}$, $Sn^{4+}$, $P^{5+}$, $As^{5+}$; X-anions are $S^{2-}$, $Se^{2-}$, $Te^{2-}$. They have been studied for a long time for their interesting physical and chemical properties [1-10]. Most of these materials are of special interest due to their phase transitions, which tak e place close to ambient temperature [11,12]. High-temperature modifications, as a rule, crystallize in a cubic structure and have high ionic conductivity. Especially, copper and silver-containing compounds of this family are well-known superionic semiconductors due to the presence of highly mobile $Cu^+$ and $Ag^+$ ions [13-18]. The tendency of argyrodite phases to undergo multiple phase transitions indicates closely competing thermodynamic states as temperature increases. The thermodynamic characteristics of these transitions for some compounds of the argyrodite family were determined by the EMF method with a solid electrolyte in [19-22]. In [23-25], we studied a number of argyrodite compounds using differential scanning calorimetry (DSC), which is considered to be one of the accurate methods in thermal analysis.

*The purpose* of this work was to determine the thermodynamic functions of the phase transition of the $Cu_8GeSe_6$ compound using the DSC method and compare it with similar data for other compounds of the argyrodite family.

The $Cu_8GeSe_6$ compound melts with decomposition at 1083 K and has a phase transition at 333 K [26] (328 K according to [27]). The low-temperature modification LT-$Cu_8GeSe_6$ crystallizes in a hexagonal crystal lattice (Space Group $P6_3mc$; a = 12.6438(2) Å; c = 11.7570(1) Å) [26, 27], and the high-temperature HT- $Cu_8GeSe_6$ has a cubic structure (Space group *F-43m*; a=10.20 Å) [28].

The thermodynamic properties of the $Cu_8GeSe_6$ compound were studied in [22] using the EMF method with the $Cu_4RbCl_3I_2$ solid electrolyte and the partial and integral thermodynamic functions of both its crystalline modifications were determined. Next, by combining the obtained data, the thermodynamic functions of the polymorphic transition of this compound were calculated.

## Experimental part

The $Cu_8GeSe_6$ compound was synthesized by direct alloying of stoichiometric amounts of elemental components of high purity (99.9999%) from *Evochem Advanced Materials GMBH (Germany)*. The synthesis was carried out in evacuated (~$10^{-2}$ Pa) and sealed quartz ampoules at a temperature of ~1150 K. Taking into account the high elasticity of selenium vapor at the melting temperature of $Cu_8GeSe_6$, the synthesis was carried out in a two-zone mode. After synthesis, the sample was annealed at 770 K (100 h). Next, the ampoule was cooled very slowly in the region of the temperature of the polymorphic transformation of the compound (320-370 K), and then subjected to thermal annealing at 320 K (10 hours). This was done in order to ensure a complete transition of the high-temperature phase to the low-temperature phase in order to minimize the error in enthalpy calculations. The synthesized compound was identified by differential thermal (DTA) and X-ray diffraction analysis (XRD). The thermal effect temperatures in the DTA heating curve were in accordance with the above literature data. XRD was carried out at room temperature on a D8 ADVANCE powder diffractometer with CuK$\alpha_1$ radiation from *Bruker*. The powder diffraction pattern of the compound (**Fig. 1**) confirmed the complete transition of the compound to the low-temperature structure.

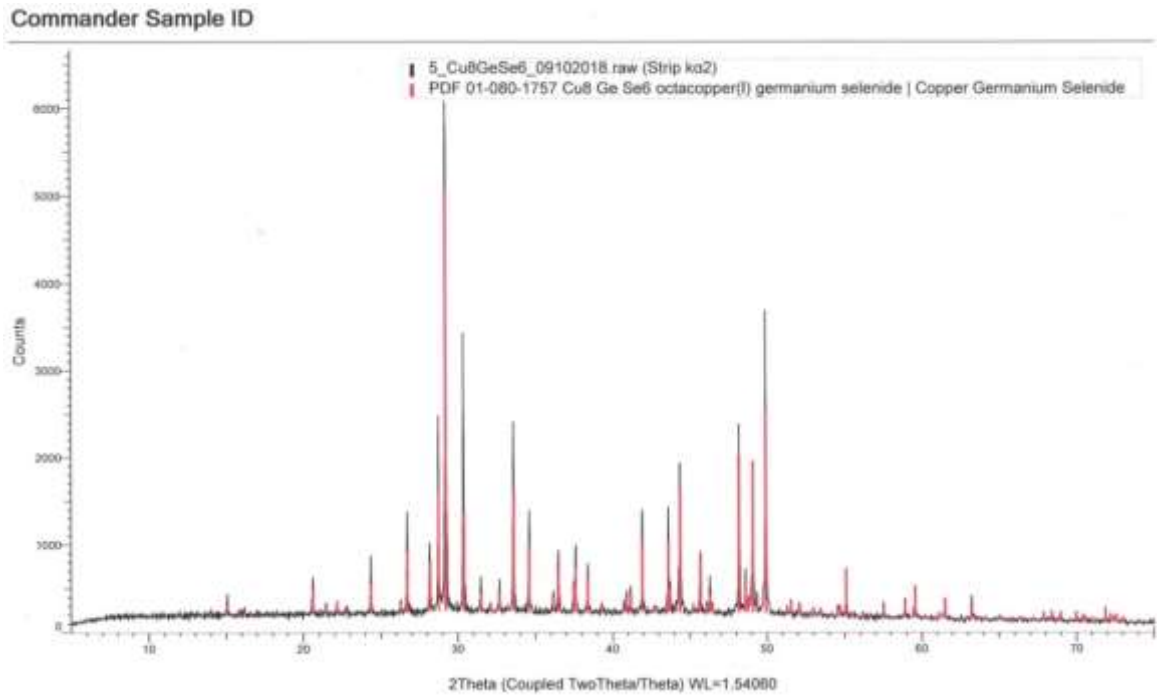


**Fig.1.** Powder diffraction pattern of the $Cu_8SiSe_6$ compound

As can be seen from **Fig. 1**, the reflection peaks we obtained for the synthesized $Cu_8GeSe_6$ completely coincide with the X-ray data (*red lines*) of the hexagonal structure of this

compound from the crystallographic database (*Powder Diffraction File 01-080-1757*).

The temperature and heat of phase transition of the $Cu_8SiSe_6$ compound were determined using the DSC method on a differential scanning calorimeter DSC400 from *Linseis* (Germany). The calorimeter was previously calibrated. The measurements were carried out using the *Linseis TA V 2.3.1* program. The heating rate was 3°/min. The process of calorimeter calibration and measurements are described in detail in our previous similar works [23-25].

## Results and discussion

In order to improve the accuracy of the study, two samples of the $Cu_8SiSe_6$ compound with sample masses of 33.17 and 37.25 mg were selected. For each sample, 3 DSC curves were recorded in a dynamic heating mode from room temperature to ~400 K.

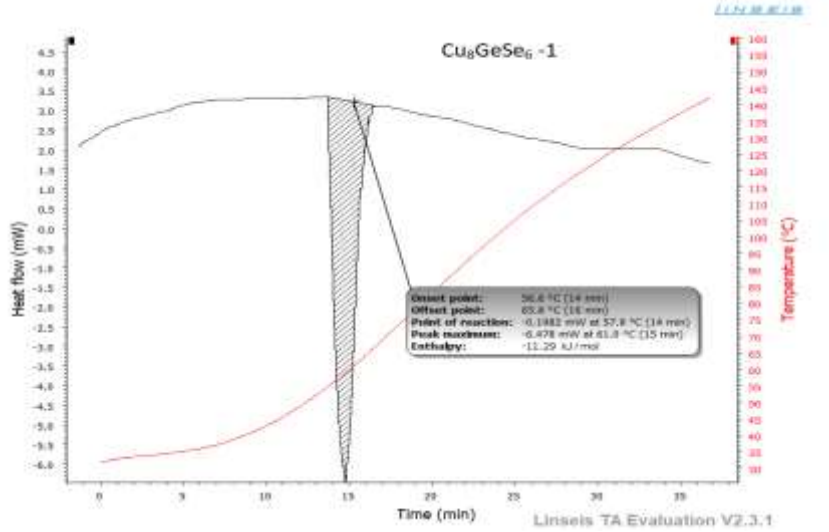


**Fig. 2.** DSC heating curve for the $Cu_8GeSe_6$; sample weight 33.17 mg

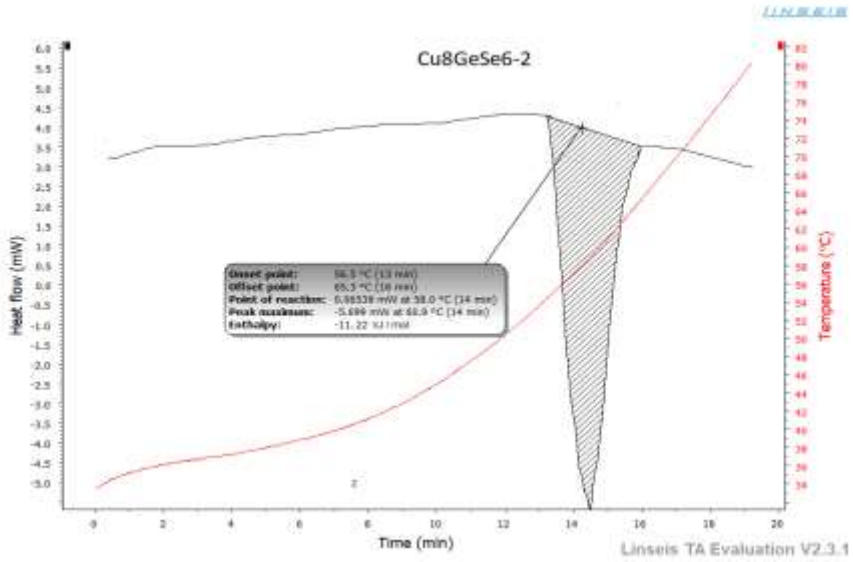


**Fig. 3.** DSC heating curve for the $Cu_8GeSe_6$; sample weight 37.25 mg

Next, the temperatures of the beginning and end of the peak, as well as the enthalpy of phase transition ($\Delta H_{p.t}$) were determined per 1 mole of studied substance. For example, Figures 2 and 3 show DSC heating curves for samples with masses of 33.17 and 37.25 mg,

respectively. The data on all six DSC curves were nearly identical and differed by no more than 2%. According to [29, 30], in such cases, the error in determining thermal effects is no more than ±4%.

The average value of the experimentally obtained values of the heat of polymorphic transformation was taken as the final value $\Delta H_{p.t}$ (**Table**).

Using the combined equation of the 1st and 2nd laws of thermodynamics and taking into account the phase transitions $\Delta G_\alpha = \Delta G_\beta$, the following relation for the entropy of the phase transition was obtained:

$$\Delta S_{p.t.} = \Delta H_{p.t.}/T_{p.t.}$$

Using the last equation and the values of the enthalpy of the phase transition of the substance and the temperature of the onset of the peak (330 K) from the DSC data, we calculated the entropy of the phase transition of the compound under study (**Table**).

**Table.** Temperatures and thermodynamic functions of phase transitions of argyrodite family compounds

| **Compound** | **$T_{p.t.}$,** *K* | **$\Delta H_{p.t.}$,** *kJ·mol$^{-1}$* | **$\Delta S_{p.t.}$,** *J·mol$^{-1}$·K$^{-1}$* | **Ref., method** |
|---|---|---|---|---|
| $Cu_8SiS_6$ | 336 | 14.85±0.59 | 44.20±1.77 | [23], DSC |
| $Cu_8SiSe_6$ | 325 | 14.73±0.59 | 45.32±1.81 | [24], DSC |
| $Cu_8GeS_6$ | 330 | 15.54±0.62 | 47.09±2.88 | [23], DSC |
| | | 12.4±5.1 | 37.8±14.1 | [22], EMF |
| $Cu_8GeSe_6$ | 330 | 11.23±0.45 | 34.03±1.36 | ***This work***, DSC |
| | | 11.9±2.8 | 35.5±8.4 | [22], EMF |
| $Ag_8GeS_6$ | 495 | 9.46±0.38 | 19.11±0.76 | [25], ДСК |
| $Ag_8GeSe_6$ | 320 | 15.4±4.7 | 46.9±14.8 | [19], EMF |
| | 321 | 16.95±0.68 | 52.80±2.11 | [25], DSC |
| $Ag_8SnS_6$ | 446 | 8.77±0.35 | 19.66±0.79 | [25], DSC |
| $Ag_8SnSe_6$ | 355 | 15.4±4.3 | 43.4±12.1 | [20], EMF |
| | | 19.67±0.60 | 55.41±2.22 | [25], DSC |

The **Table** also shows thermodynamic functions of phase transitions for other argyrodite family compounds, obtained by two different methods. As can be seen, for the $Cu_8GeSe_6$ compound these values are close. The obtained data for other analogs are somewhat different. It should be noted, that calorimetric data are the results of direct measurement of heat flow and have a fairly high accuracy. The relatively high errors in the data obtained by the EMF method are due to the fact that in this method the heat of phase transition is determined from the differences in the slopes of the temperature dependences straight of the EMF of concentration relative to the copper (or silver) electrode cells for two modifications of studied compounds.

In addition, it should be noted that the enthalpy and entropy values of phase transformations of argyrodite compounds are abnormally high as compared to conventional polymorphic transitions. This is explained as being due to higher degree of disorder in the structure of argyrodite compounds during the phase transformation. During the transition to the high-temperature modification, a rigid anionic frame is formed, which has many empty positions, due to which copper (or silver) cations acquire high mobility. This leads to an additional increase in entropy.

**Acknowledgment**

*This work supported by the Azerbaijan Science Foundation –* ***Grant No AEF-MCG-2022-1(42)-12/10/4-M-10****.*

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## КАЛОРИМЕТРИЧЕСКОЕ ИССЛЕДОВАНИЕ ФАЗОВОГО ПЕРЕХОДА $Cu_8GeSe_6$ И СРАВНЕНИЕ С ДРУГИМИ СОЕДИНЕНИЯМИ СЕМЕЙСТВА АРГИРОДИТА

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**Аннотация:** Данная работа является продолжением наших работ по термодинамическому исследованию синтетических аналогов минерала аргиродита. Методом дифференциальной сканирующей калориметрии (ДСК) проведено калориметрическое исследование фазового перехода соединения $Cu_8GeSe_6$. По данным кривых ДСК образцов исследуемого соединения различной массы определены температура и энтальпия фазового перехода от низкотемпературной орторомбической модификации к высокотемпературной кубической модификации. С помощью уравнения Гиббса-Гельмгольца также была рассчитана энтропия фазового перехода. Проведен сравнительный анализ полученных термодинамических значений исследуемого соединения с другими аргиродитами.
**Ключевые слова:** фазовый переход, термодинамические функции, селенид меди-германия, дифференциальная сканирующая калориметрия.

## $Cu_8GeSe_6$ BİRLƏŞMƏSİNİN FAZA KEÇİDİNİN KALORİMETRİK TƏDQİQİ VƏ ARQİRODİT AİLƏSİNİN DİGƏR BİRLƏŞMƏLƏRİ İLƏ MÜQAYİSƏSİ

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**Xülasə:** Bu iş bizim argirodit mineralının sintetik analoqlarının termodinamik tədqiqi üzrə apardığımız işlərin davamıdır. $Cu_8GeSe_6$ birləşməsinin faza keçidinin kalorimetrik tədqiqi diferensial skanedici kalorimetriya (DSK) üsulu ilə aparılmışdır. Tədqiq olunan birləşmənin müxtəlif kütləli nümunələrinin DSK əyriləri əsasında aşağı temperaturlu ortorombik modifikasiyadan yüksək temperaturlu kubik fazaya keçid temperaturu və entalpiyası müəyyən edilmişdir. Faza keçidinin entropiyası da Gibbs-Helmholtz tənliyi ilə hesablanmışdır. Tədqiq olunan

birləşmənin əldə edilmiş termodinamik qiymətlərinin digər argiroditlərlə müqayisəli təhlili aparılmışdır.

**Açar sözlər:** faza keçidi, termodinamik funksiyalar, mis-germanium selenid, diferensial skanedici kalorimetriya.