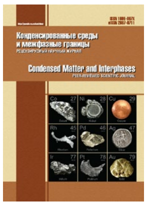

ISSN 1606-867X (Print)
ISSN 2687-0711 (Online)
Condensed Matter and Interphases
Kondensirovannye Sredy i Mezhfaznye Granitsy
https://journals.vsu.ru/kcmf/

Original articles

Research article
https://doi.org/10.17308/kcmf.2022.24/9258

Calorimetric determination of phase transitions of Ag_8BX_6 (B = Ge, Sn; X = S, Se) compounds

U. R. Bayramova, A. N. Poladova, L. F. Mashadiyeva, M. B. Babanly✉

*M. Nagiev Institute of Catalysis and Inorganic Chemistry of the Azerbaijan National Academy of Sciences,
113, H. Javid pr., Baku Az1143, Azerbaijan*

Abstract

Differential scanning calorimetry (DSC) was used to study ternary Ag_8GeS_6, Ag_8GeSe_6, Ag_8SnS_6, and Ag_8SnSe_6 compounds which undergo polymorphic transformations at relatively low temperatures. Two samples of each compound with different masses in the range of 20-40 mg were examined and three DSC heating curves were taken for each sample. The DSC curve data were used to determine the temperatures and enthalpies of the phase transitions of the studied compounds from a low-temperature rhombic modification to a high-temperature cubic modification. The difference in the DSC data between all samples and all heating curves did not exceed 2%. The obtained data were used to calculate the entropies of phase transitions. It was shown that these values are abnormally high. The study also involved a comparative analysis of the obtained thermodynamic data for the Ag_8GeSe_6 and Ag_8SnSe_6 compounds and the results obtained by the method of electromotive forces.

Keywords: Ag_8GeS_6, Ag_8GeSe_6, Ag_8SnS_6, Ag_8SnSe_6, phase transition, thermodynamic functions, enthalpy, entropy, differential scanning calorimetry

Funding: The study was supported by the Science Development Foundation under the President of the Republic of Azerbaijan within the grant EİF-BGM-4-RFTF-1/2017- 21/11/ 4-M-12.

For citation: Bayramova U. R., Poladova A. N., Mashadiyeva L. F., Babanly M. B. Calorimetric determination of phase transitions of Ag_8BX_6 (B = Ge, Sn; X = S, Se) compounds. *Condensed Matter and Interphases.* 2022;24(2): 187–195. https://doi.org/10.17308/kcmf.2022.24/9258

Для цитирования: Байрамова У. Р., Поладова А. Н., Машадиева Л. Ф., Бабанлы М. Б. Калориметрическое определение фазовых переходов соединений Ag_8BX_6 (B = Ge, Sn; X = S, Se). *Конденсированные среды и межфазные границы*. 2022;24(2): 187–195. https://doi.org/10.17308/kcmf.2022.24/9258

✉ Mahammad Babanly, email: babanlymb@gmail.com

1. Introduction

The argyrodite family compounds with the general formula $A_8B^{IV}X_6$ (where A – Cu, Ag; B^{IV} – Si, Ge, Sn; X – S, Se, Te) have a number of valuable functional properties and have been studied by many research teams [1–3]. These compounds are attracting more and more attention as promising candidates for thermoelectric materials due to their excellent transport properties, relatively low thermal conductivity [4–13]. Moreover, their components are widely commonand low-toxic . Many of these compounds undergo phase transitions at relatively low temperatures (310–520 K). Typically, high-temperature modifications crystallise in a cubic structure, and low-temperature phases have lower symmetry. Most of the high-temperature phases of these compounds, due to the peculiarities of their crystal structure, have mixed electron-ion conductivity and demonstrate high values of cationic conductivity and ionic diffusion for solids due to the high mobility of copper (or silver) ions in the “liquid-like” ion sublattice [14-20]. This makes them promising materials for ion-selective electrodes and solid electrolytes when developing various types of electric batteries, sensors, etc. [14–22].

The purpose of this work was to determine the thermodynamic functions of phase transitions of Ag_8GeS_6, Ag_8GeSe_6, Ag_8SnS_6, and Ag_8SnSe_6 compounds by differential scanning calorimetry (DSC). This method is considered to be one of the most advanced and highly sensitive methods of phase analysis. What is more, modern DSC devices have a wide range of capabilities that can be used to determine not only the temperature and enthalpy of phase transformations, heat capacity, and its dependence on thermodynamic parameters, but also the kinetic characteristics of physicochemical processes under the conditions of linear temperature change [23].

The nature of melting and the crystalline structures of the objects of our study have been examined in detail. The silver-germanium chalcogenides Ag_8GeS_6 and Ag_8GeSe_6 melt congruently at 1.228 K and 1.175 K and undergo polymorphic transformations at 493 K and 321 K, respectively [24–26]. The Ag_8SnS_6 and Ag_8SnSe_6 compounds also melt congruently at 1,112 K and 1,015 K and undergo polymorphic transformations at 445 K and 356 K, respectively [24, 27]. Low-temperature modifications (LT) of all studied compounds have rhombic structures, while their high-temperature (HT) modifications have cubic structures [24, 28–32]. More detailed information on the parameters of the crystal lattice of the above-mentioned compounds is given in Table 1.

The thermodynamic properties of the studied compounds have been investigated in a number of papers [33–37]. In [33–35], the EMF method with a glassy Ag^+ conductive electrolyte in the

Table 1. Crystallographic data for the Ag_8GeS_6, Ag_8GeSe_6, Ag_8SnS_6, and Ag_8SnSe_6 compounds

Compound	Phase Transition Temperature, K	Crystallographic data
Ag_8GeS_6	493	HT rhombic phase; space group: $Pna2_1$; a = 15.149 Å; b = 7.476 Å; c = 10.589 Å [28]
		HT cubic phase; space group: *F*-43*m*; a = 10.70 Å [24]
Ag_8GeSe_6	321	HT rhombic phase; space group: $Pmn2_1$; a = 7.823 Å, b = 7.712 Å, c = 10.885 Å [29]
		HT cubic phase; space group: *F*-43*m;* a = 10.99 Å [24]
Ag_8SnS_6	445	HT rhombic phase; space group: $Pna2_1$; a = 15.2993(9)Å; b = 7.5479(4); c = 10.7045(6) [31]
		HT cubic phase; space group: *F*-43*m;* a = 10.85 Å [24]
Ag_8SnSe_6	356	HT rhombic phase; space group: $Pmn2_1$; a = 7.89052(6) Å; b = 7.78976(6) Å; c = 11.02717(8) Å [2]
		HT cubic phase; space group: *F*-43*m;* a = 11.12 Å [24, 32]

temperature range of 400–520 K was used to study the Ag-Ge-Se and Ag-Sn-Se systems and to determine the thermodynamic functions of the formation of high-temperature modifications of the Ag_8GeSe_6 and Ag_8SnSe_6 compounds. Later, we studied these systems [36, 37] in a lower temperature region (390–450 K) by the EMF method with a solid Ag_4RbI_5 electrolyte. These EMF data were used to calculate the standard integral thermodynamic functions of the formation of both crystalline modifications of the Ag_8GeSe_6 and Ag_8SnSe_6 compounds. Thermodynamic functions of their polymorphic transitions were calculated by combining the obtained data.

2. Experimental

2.1. Synthesis

The Ag_8GeS_6, Ag_8GeSe_6, Ag_8SnS_6, and Ag_8SnSe_6 compounds were synthesised for the study by direct fusion of elementary components of high purity in evacuated (~10^{-2} Pa) and sealed quartz ampoules. High-purity elementary components manufactured by Evochem Advanced Materials GmbH (Germany) were used for the synthesis: silver granules (Ag-00047; 99.999 %), germanium pieces (Ge-00003; 99.999 %), tin granules (Sn-00005; 99.999 %), sulphur pieces (S-00001; 99.999 %), and selenium granules (Se-00002; 99.999 %). Due to the high vapour pressure of sulphur and selenium at the melting temperatures of the synthesised compounds, the synthesis was carried out in a dual-zone mode. The temperature regime for the synthesis of each compound was selected with due account of their melting points and phase transformations. The ampoule with the reaction mixture was heated in an inclined tubular furnace to the temperature which exceeded by ~50° the melting point of the synthesised compound ("hot" zone). A part of the ampoule (~8 cm) was located outside the furnace and was cooled with water to control the pressure of sulphur or selenium vapours and prevent the ampoule from exploding ("cold" zone). To accelerate the interaction, the ampoule was rotated around the longitudinal axis and subjected to vibration. When the bulk of sulphur or selenium had reacted, the ampoule was introduced into the furnace completely and held in the hot zone for 1 hour. Further, the ampoule was cooled (very slowly in the region of the polymorphic transformation temperature), and then subjected to thermal annealing just below these temperatures for 10–15 hours. This was done to ensure a complete transition of the high-temperature phase to the low-temperature phase in order to minimise the error in the enthalpy calculations. High-temperature modifications for each compound were also obtained by heating the samples in evacuated and sealed ampoules to 350 °C. Then they were quenched by plunging them into ice water.

The synthesised compounds were identified by X-ray diffraction analysis (XRD). The XRD of the samples was carried out on a D8 ADVANCE powder diffractometer from Bruker (Germany) with Cu$K\alpha_1$ radiation. The powder diffraction patterns presented in Fig. 1 show that the diffraction patterns of compounds which were cooled slowly after synthesis completely coincide with the XRD data (red lines in the online version) of the low-temperature rhombic modifications from the crystallographic database. The powder diffraction patterns of the quenched samples had diffraction patterns that were completely indexed in the cubic structure. Fig. 2 shows an example of a diffraction pattern of a quenched Ag_8GeS_6 sample. Thus, the XRD results of the synthesised samples confirmed their single-phase nature.

2.2. Experimental

The temperatures and the heat of the phase transitions of the studied compounds were determined by the DSC method. The principle of this method is based on the measurement of the temperature dependence of the difference in heat flows in the substance and the reference material exposed to a temperature programme. The DSC method determines heat by the heat flow, a heat derivative with respect to time. Differential scanning calorimeters have two measuring cells: one is for the studied sample while in the other, the reference cell, an empty crucible is normally placed. The measured value is the temperature difference between the sample and the reference cells at any moment of time. As a good approximation, it can be assumed that the heat exchange between the various elements of the measuring system is only carried out by the mechanism of thermal conductivity. According to the thermal conductivity equation, the

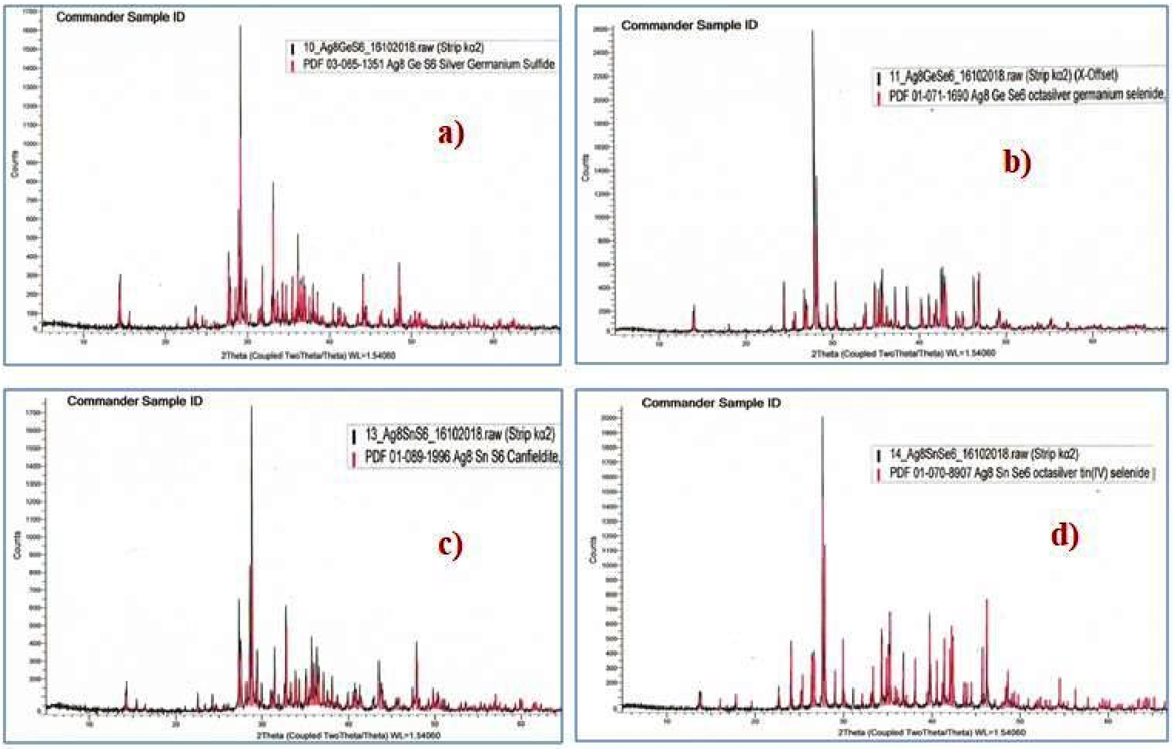

Fig. 1. Powder diffraction patterns of low-temperature modifications of the Ag_8GeS_6 (*a*), Ag_8GeSe_6 (*b*), Ag_8SnS_6 (*c*), and Ag_8SnSe_6 (*d*) compounds

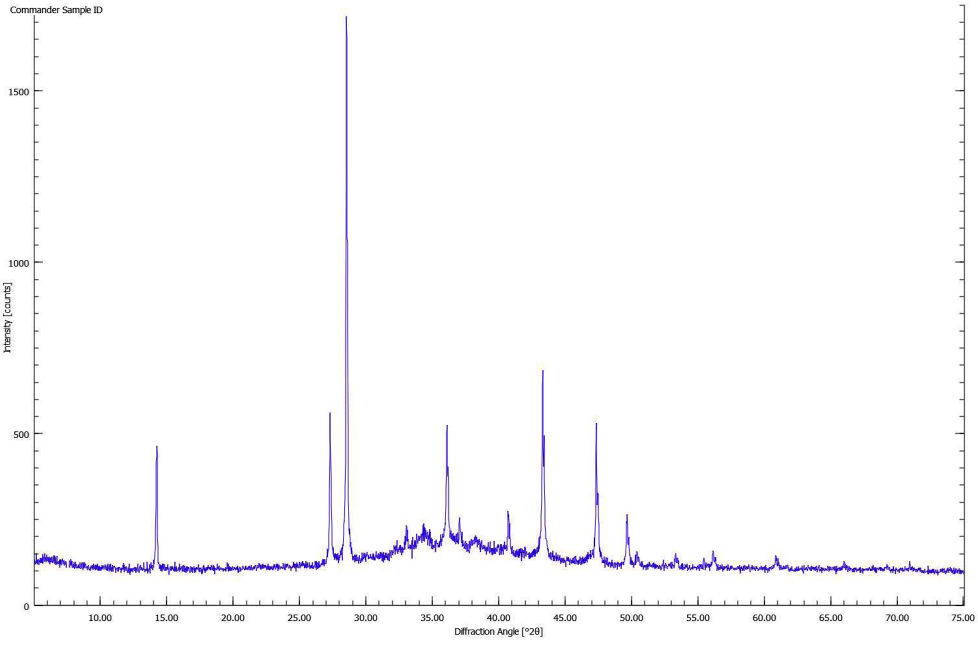

Fig. 2. Powder diffraction pattern of the Ag_8GeSe_6 sample, quenched from 350 °C

temperature difference measured at two points at the same moment of time is proportional to the value of the heat flow between them. The differential signal is displayed as a reference line. Effects, such as phase transitions of the first order, can be observed in the form of a peak. The area of the peak is the amount of enthalpy, and the direction of the peak indicates the direction of heat flow, endothermic or exothermic [23].

Three characteristic temperatures can be used to describe the peak on the DSC curve: T_{onset}, T_{peak}, and T_{end} (Fig. 3). The initial and final temperatures correspond to the intersection of the reference line extrapolated to the peak region

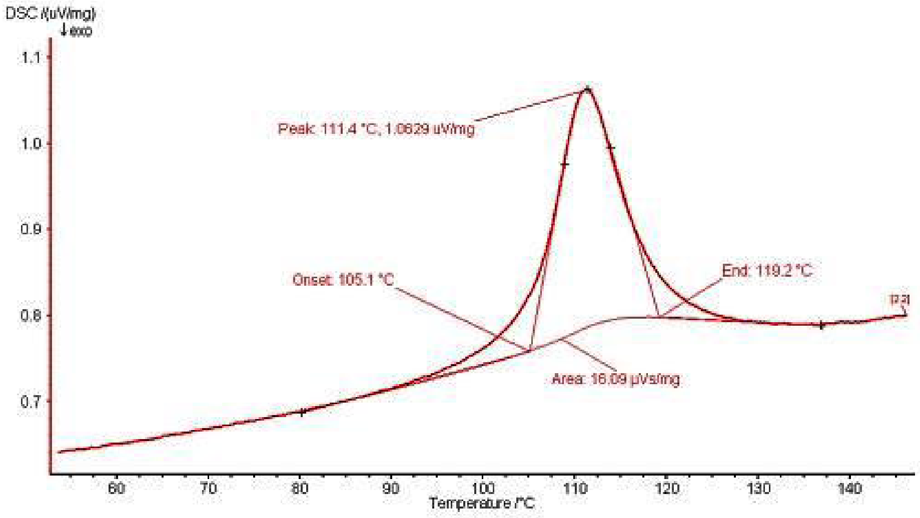

Fig. 3. Characteristics of the peak on the DSC curve

and the tangents drawn through the point of inflexion. The reference line is a virtual line drawn through the interval in which a reaction or phase transition occurs under the assumption that the heat of the process is zero.

Our experiments were carried out on a DSC400 differential scanning calorimeter manufactured by Linseis (Germany), which had the following specifications:

· Temperature range of the platinum furnace: from room temperature to 1,600 °C.

· Temperature scanning speed: in the range from 0.01 to 100 °C/min.

· Thermocouples: platinum-platinum-rhodium.

· Temperature accuracy: 0.01°.

· DSC resolution: 1 mW.

· Calorimetric sensitivity: 17.6 µW.

· Heat accuracy: ±1 %.

The measurements were taken using the Linseis TA V 2.3.1 software. The calorimeter had been pre-calibrated. Since our studies were carried out at low temperatures (300–550 K), relatively low-melting metals were used as references for the calibration of our device: indium, tin, bismuth, and zinc provided by Linseis for this purpose, with appropriate certificates. The calibration temperature for each substance was selected in accordance with the recommendations given in the manual.

The DSC of the compounds and references was performed using an aluminium crucible with a lid. Given that the studied compounds were solid polycrystalline samples, they were preliminarily ground to a powdery state prior to the measurement in order to ensure the maximum contact area between the studied sample and the crucible bottom. Due to the fact that the amount of the sample tested by the DSC method was very small (about several tens of mg), a greater weighing error could lead to a very noticeable relative error in determining the extensive values. Therefore, to weigh the samples, we used accurate (first class of accuracy according to GOST) Radwag electronic analytical balance (Poland), AS220 series, with a range from 1 mg to 220 g and a measurement accuracy of 0.01/0.1 mg. The DSC study mode was selected based on the phase transition temperature of the studied compound. The heating rate was 3 °/min. The measurements were carried out in a flow of argon.

3. Results and Discussion

To determine the temperatures and enthalpies of the phase transitions of the Ag_8GeS_6, Ag_8GeSe_6, Ag_8SnS_6, and Ag_8SnSe_6 compounds, we took DSC heating curves for the samples. Two samples of each compound with different masses in the range of 20–40 mg were selected and three DSC heating curves were taken for each sample. Thus, 6 DSC curves were taken for each compound. The DSC curves were then processed using the Linseis TA Evaluation V2.3.1 software and the temperatures of the beginning and the end of the peak and the enthalpy of the phase transition for 1 mole of substance were obtained. These values were almost identical in the DSC curves for all samples and the difference did not exceed 2%. According to [38], in such cases, the error in determining the thermal effects is not more than ±4%.

Below, as an example, we present the study and calculation procedure for the Ag_8SnSe_6 compound. We selected two samples of this compound with masses of 25.56 and 33.72 mg. Given that the phase transition temperature for the Ag_8SnSe_6 compound is 356 K [24], the DSC study was carried out in a dynamic mode of heating from room temperature to 400 K. The DSC heating curve obtained for the Ag_8SnSe_6 sample with a mass of 25.56 mg is shown in Fig. 4. The following average values of phase transition enthalpies were obtained: D$H_{p.t}$ = 19.63 kJ/mol (25.56 mg); D$H_{p.t}$ = 19.71 kJ/mol (33.72 mg). The average for these values was taken as the final value of D$H_{p.t.}$ for the Ag_8SnSe_6 compound (Table 2).

Table 2 also shows the temperatures and average values for phase transition enthalpies for

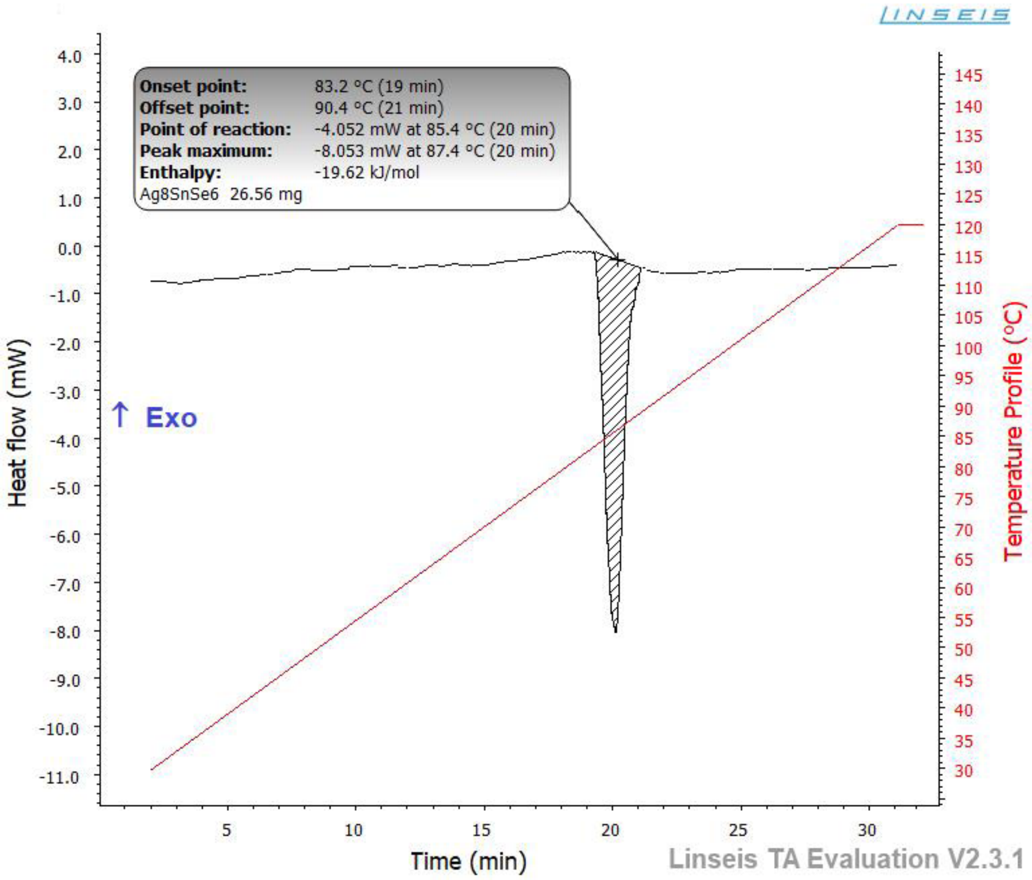

Fig. 4. DSC heating curve of the Ag_8SnSe_6 compounds with a mass of 26.56 mg

Table 2. Thermodynamic data for phase transitions of the Ag_8GeS_6, Ag_8GeSe_6, Ag_8SnS_6, and Ag_8SnSe_6 compounds

Compound	Phase Transition Temperature, K	$\Delta H_{p.t}$, кJ/mol	$\Delta S_{p.t.}$, J/(mol×K)
Ag_8GeS_6	495	9.46±0.38	19.11±0.76
Ag_8GeSe_6	321	16.95±0.68	52.80±2.11
		15.0±4.7 [36]	46.9±14.8 [36]
Ag_8SnS_6	446	8.77±0.35	19.66±0.79
Ag_8SnSe_6	355	19.67±0.6	55.41±2.22
		15.4±4.3 [37]	43.4±12.1 [37]

the rest of the studied compounds. The obtained values of enthalpies and temperatures (T_{onset}) of phase transitions were used to calculate entropies of phase transitions (Table 2) by the formula:

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

As shown in Table 2, the entropy values of the phase transitions of the two sulphide compounds are very close. Apparently, this is due to the fact that these values refer to the same type of change in the crystal structure during the phase transition (from a rhombic lattice to a cubic lattice). In other words, the degree of disordering at the phase transition is approximately the same for both compounds. A similar pattern was also observed for selenides. It should be noted that selenides had much higher values of $DS_{p.t}$ than sulphides. This indirectly indicates a greater disordering of silver ions in the cubic lattice of selenides as compared to sulphides.

It should be noted that the values of $\Delta H_{\text{p.t}}$ for the Ag_8GeSe_6 and Ag_8SnSe_6 compounds [36, 37] obtained by the EMF method differ from the results of this work by up to 22%, which is within the error of the data obtained by the EMF method (Table 2). It is obvious that the calorimetric data are more accurate, since the EMF method determines the heat of the phase transition from the differences in the slopes of the lines of the direct EMF temperature dependencies for the two modifications [39, 40].

The analysis of the published data on thermodynamic functions of phase transitions of chalcogenides [41] showed that the values of such functions for our research objects are quite high compared to the values of thermodynamic functions of phase transitions of the first kind. Apparently, this is due to a higher degree of disordering in their structure during phase transformation. During the transition to the high-temperature modification of the argyrodite-type $Ag_8B^{IV}X_6$ compounds, many empty positions are formed in the rigid anionic framework, which makes silver cations mobile [14, 24]. This leads to an additional growth in entropy.

4. Conclusions

We provided new data on the thermodynamic functions of phase transitions of Ag_8GeS_6, Ag_8GeSe_6, Ag_8SnS_6, and Ag_8SnSe_6 compounds, members of the argyrodite family, obtained by DSC. The abnormally high entropy values for the phase transitions characteristic of these compounds can be explained by strong disordering in the cationic sublattice of high-temperature cubic modifications, which is accompanied by an increased mobility of silver ions.

Author contributions

M. B. Babanly: scientific supervision, research concept, and conclusions. L. F. Mashadiyeva: research concept, writing of the article, discussion of the results. U. R. Bayramova, A. N. Poladova: synthesis of the compounds, research.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

References

1. Babanly M. B., Yusibov Yu. A., Abishov V. T. *Ternary chalcogenides based on copper and silver*. Baku: BQU Publ.; 1993. 342 p. (In Russ.)

2. Semkiv I., Ilchuk H., Pawlowski M., Kusnezh V. Ag_8SnSe_6 argyrodite synthesis and optical properties. *Opto-Electronics Review*. 2017;25(1): 37–40. https://doi.org/10.1016/j.opelre.2017.04.002

3. Studenyak I. P., Pogodin A. I., Studenyak V. I., Izai V. Y., Filep M. J., Kokhan O. P., Kúš P. Electrical properties of copper- and silver-containing superionic $(Cu_{1-x}Ag_x)_7SiS_5I$ mixed crystals with argyrodite structure. *Solid State Ionics*. 2020;345: 115183. https://doi.org/10.1016/j.ssi.2019.115183

4. Lin S., Li W., Pei Y. Thermally insulative thermoelectric argyrodites. *Materials Today*. 2021;48:198–213. https://doi.org/10.1016/j.mattod.2021.01.007

5. Shen X., Yang C., Liu Y., Wang G., Tan H. A High temperature structural and thermoelectric study of argyrodite Ag_8GeSe_6. *ACS Applied Materials & Interfaces*. 2019;11(2): 2168–2176. https://doi.org/10.1021/acsami.8b19819

6. Jin M., Lin S., Li W., Chen Z., Li R., Wang X. Pei Y. Fabrication and thermoelectric properties of single-crystal argyrodite Ag_8SnSe_6. *Chemistry of Materials*. 2019;31(7): 2603–2610. https://doi.org/10.1021/acs.chemmater.9b00393

7. Jiang B., Qiu P., Eikeland E., Chen H., Song Q., Ren D., Chen L. Cu_8GeSe_6-based thermoelectric materials with an argyrodite structure. *Journal of Materials Chemistry C*. 2017;5(4): 943–952. https://doi.org/10.1039/C6TC05068A

8. Jiang Q., Li S., Luo Y., Xin J., Li S., Li W., Yang J. Ecofriendly highly robust Ag_8SiSe_6-based thermoelectric composites with excellent performance near room temperature. *ACS Applied Materials & Interfaces*. 2020;12(49): 54653–54661. https://doi.org/10.1021/acsami.0c15877

9. Fan Y., Wang G., Wang R., Zhang B., Shen X., Jiang P., Zhang X., Gu H., Lu X., Zhou X. Enhanced thermoelectric properties of *p*-type argyrodites Cu_8GeS_6 through Cu vacancy. *Journal of Alloys and Compounds*. 2020;822: 153665. https://doi.org/10.1016/j.jallcom.2020.153665

10. Yang C., Luo, Y., Li X., Cui J. N-type thermoelectric Ag_8SnSe_6 with extremely low lattice thermal conductivity by replacing Ag with Cu. *RSC Advances*. 2021;11: 3732–3739. https://doi.org/10.1039/D0RA10454J

11. Li W., Lin S., Ge B., Yang J., Zhang W., Pei Y. Low sound velocity contributing to the high thermoelectric performance of Ag_8SnSe_6. *Advanced Sciences*. 2016;3(11): 1600196–1600212. https://doi.org/10.1002/advs.201600196

12. Ghrib T., Al-Otaibi A. L., Almessiere M. A., Assaker I. B., Chtourou R. High thermoelectric figure of merit of Ag_8SnS_6 component prepared by electrodeposition technique. *Chinese Physics Letters*. 2015;32(12): https://doi.org/10.1088/0256-307X/32/12/127402

13. Namiki H., Yahisa D., Kobayashi M., Shono A., Hayashi H. Enhancement and manipulation of the thermoelectric properties of n-type argyrodite Ag_8SnSe_6 with ultralow thermal conductivity by controlling the carrier concentration through Ta doping. *AIP Advances*. 2021; 11: 075125. https://doi.org/10.1063/5.0056533

14. Ivanov-Shits A. K., Murin I. V. *Solid state ionics, v. 1*. Saint Peterburg: SPU Publ.; 2000. 616 p. (In Russ.)

15. Berezin V. M., Vyatkin Q. P. *Superionic semiconducting chalcogenides*. Celyabinsk: Yu.Ur.Qu. Publ.; 2001. 135 p. (In Russ.)

16. Liu H., Shi X., Xu F. et al. Copper ion liquid-like thermoelectrics. *Nature Materials*. 2012;11(5): 422–425. https://doi.org/10.1038/nmat3273

17. Heep B. K., Weldert K. S., Krysiak Y., Day T. W., Zeier W. G., Kolb U., Snyder G. J., Tremel W. High electron mobility and disorder induced by silver ion migration lead to good thermoelectric performance in the argyrodite Ag_8SiSe_6. *Chemistry of Materials*. 2017;29(11): 4833–4839. https://doi.org/10.1021/acs.chemmater.7b00767

18. Lin Y., Fang S., Su D., Brinkman K. S. Enhancing grain boundary ionic conductivity in mixed ionic–electronic conductors. *Nature Communications*. 2015;6(1): 1–9. https://doi.org/10.1038/ncomms7824

19. Boucher F., Evain M., Brec R. Distribution and ionic diffusion path of silver in γ-Ag_8GeTe_6: A temperature dependent anharmonic single crystal structure study. *Journal of Solid State Chemistry*. 1993;107(2): 332–346. https://doi.org/10.1006/jssc.1993.1356

20. Heep B. K., Weldert K. S., Krysiak Y., Day T. W., Zeier W. G., Kolb U., Snyder G. J., Tremel W. High electron mobility and disorder induced by silver ion migration lead to good thermoelectric performance in the argyrodite Ag_8SiSe_6. *Chemistry of Materials*. 2017;29(11): 4833–4839. https://doi.org/10.1021/acs.chemmater.7b00767

21. Babanly M. B., Yusibov Yu. A., Babanly N. B. The EMF method with solid-state electrolyte in the thermodynamic investigation of ternary copper and silver chalcogenides. Electromotive force and measurement in several systems. *Electromotive Force and Measurement in Several Systems*. 2011;57-78: https://doi.org/10.5772/28934

22. Babanly M. B., Mashadiyeva L. F., Babanly D. M. et al. Some aspects of complex investigation of the phase equilibria and thermodynamic properties of the ternary chalcogenid systems involving EMF Measurements (Review). *Russian Journal of Inorganic Chemistry*. 2019;64(13): 1649–1671. https://doi.org/10.1134/s0036023619130035

23. Menczel J., Grebowicz J. *The handbook of differential scanning calorimetry: Techniques and low molecular mass materials*. Elsevier Science; 2022. 858 p.

24. Gorochov O. Les composés Ag_8MX_6 (M = Si, Ge, Sn et X = S, Se, Te). *Bulletin de la Société chimique de France*. 1968; 2263–2275.

25. Prince A., *Silver–germanium–selenium, in Ternary Alloys: A Comprehensive Compendium of Evaluated Con stitutional Data and Phase Diagrams*. Stuttgart: Max Plank Inst.; 1992. 492 p.

26. Yusibov Y. A., Alverdiev I. D., Ibragimova F. S., Mamedov A. N., Tagiev D. B., Babanly M. B. Study and 3d modeling of the phase diagram of the Ag–Ge–Se system. *Russian Journal of Inorganic Chemistry*. 2017;62(9): 1223–1233. https://doi.org/10.1134/S0036023617090182

27. Yusibov Y. A., Alverdiev I. D., Mashadieva L. F., Babanly D. M., Mamedov A. N., Babanly M. B. Experimental study and 3d modeling of the phase diagram of the Ag–Sn–Se System. *Russian Journal of Inorganic Chemistry*. 2018;63(12): 1622–1635. https://doi.org/10.1134/S0036023618120227

28. Eulenberger G. Die kristallstruktur der tieftemperaturmodifikation von Ag_8GeS_6. *Monatshefte Fur Chemie*. 1977;108(4): 901–913. https://doi.org/10.1007/bf00898056

29. Carré D., Ollitrault Fichet R., Flahaut J. Structure de $Ag_8GeSe_6β$. *Acta Crystallographica Section B Structural Crystallography and Crystal Chemistry*. 1980;36(2): 245–249. https://doi.org/10.1107/S0567740880003032

30. Wang N. New data for Ag_8SnS_6 (canfeildite) and Ag_8GeS_6 (argyrodite). *Neues Jahrb. Mineral., Monatsh;*1978; 269–272.

31. Slade T. J., Gvozdetskyi V., Wilde J. M., Kreyssig A., Gati E., Wang L., Mudryk Y., Ribeiro R. A., Pecharsky V. K., Zaikina J. V., Bud'ko S. L., Canfield P. C. A low-temperature structural transition in canfieldite, Ag_8SnS_6, single crystals. *Inorganic Chemistry*. 2021;60(24): 19345–19355. https://doi.org/10.1021/acs.inorgchem.1c03158

32. Gulay L. D., Olekseyuk I. D., Parasyuk O. V. Crystal structure of β-Ag_8SnSe_6. *Journal of Alloys and Compounds*. 2002; 339(1): 113–117. https://doi.org/10.1016/s0925-8388(01)01970-3

33. Moroz M. V., Prokhorenko M. V. Determination of thermodynamic properties of saturated solid solutions of the Ag–Ge–Se system using EMF technique. *Russian Journal of Electrochemistry*. 2015;51(7): 697–702. https://doi.org/10.1134/S1023193515070046

34. Moroz M. V., Prokhorenko M. V. Measurement of the thermodynamic properties of saturated solid solutions of compounds in the Ag-Sn-Se system by the EMF method. *Russian Journal of Physical Chemistry A*. 2015;89(8): 1325–1329. https://doi.org/10.1134/s0036024415080221

35. Moroz M. V., Prokhorenko M. V., Demchenko P. Yu., Reshetnyak O. V. Thermodynamic properties of saturated solid solutions of Ag_7SnSe_5Br and Ag_8SnSe_6 compounds in the Ag–Sn–Se–Br system measured by the EMF method. *The Journal of Chemical Thermodynamics*. 2017;106; 228–231. https://doi.org/10.1016/j.jct.2016.12.004

36. Alverdiev I. D., Yusibov Y. A., Bagkheri S. M., Imamalieva S. Z., Babanly M. B. Thermodynamic study of Ag_8GeSe_6 by EMF with an Ag_4RbI_5 solid electrolyte *Russian Journal of Electrochemistry*. 2017;53(5): 551–554. https://doi.org/10.1134/S1023193517050032

37. Alverdiev I. D., Yusibov Y. A., Imamalieva S. Z., Babanly D. M., Tagiev D. B., Babanly M. B. Thermodynamic study of siver-tin selenides by the EMF method with Ag_4rbi_5 solid electrolyte. *Russian Journal of Electrochemistry*. 2019;55(5): 467–474. https://doi.org/10.1134/s1023193519050021

38. Hohne G. W. H., Hemminger W. F., Flammersheim H. J. *Differential Scanning Calorimetry.* Second Edition. Berlin: Springer; 2003. 300 p. https://doi.org/10.1007/978-3-662-06710-9_3

39. Morachevskiy A. Q., Voronin Q. F., Qeyderikh V. A., Kutsenok I. B. Electrochemical research methods in thermodynamics of metallic systems. Moscow: ISK «Akademkniga» Publ.; 2003. 334 p. (In Russ.)

40. Babanly M. B., Yusibov Yu. A. Бабанлы М. Б., Юсибов Ю. А. Electrochemical methods in thermodynamics of inorganic systems. Baku: Elm Publ.; 2011. 306 p. (In Russ.)

41. *Physical and chemical properties of semiconductor substances*. Handbook. Novoselova A. V. and Lazereva V. B. (Eds.). Moscow: Nauka Publ.; 1976. 339 p. (In Russ.)

Information about authors

Ulviya R. Bayramova, PhD student, Institute of Catalysis and Inorganic Chemistry of the Azerbaijan National Academy of Sciences (Baku, Azerbaijan).

https://orcid.org/0000-0001-5096-2513

Albina N. Poladova, Junior Scientific Fellow, Institute of Catalysis and Inorganic Chemistry of Azerbaijan National Academy of Sciences (Baku, Azerbaijan).

https://orcid.org/0000-0001-9653-6675

Leyla F. Mashadiyeva, Ph.D. (Chem.), Accociate Professor, Senior Scientific Fellow, Institute of Catalysis and Inorganic Chemistry of Azerbaijan National Academy of Sciences (Baku, Azerbaijan).

https://orcid.org/0000-0003-2357-6195

Mahammad B. Babanly, Dr. Sci. (Chem.), Professor, Associate Member of the Azerbaijan National Academy of Sciences, Executive Director of the Institute of Catalysis and Inorganic Chemistry, Azerbaijan National Academy of Sciences (Baku, Azerbaijan).

https://orcid.org/0000-0001-5962-3710
babanlymb@gmail.com

Received 03.03.2022; approved after reviewing 18.03.2022; accepted for publication 15.04.2022; published online 25.06.2022.

Translated by Irina Charychanskaya
Edited and proofread by Simon Cox