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Study into melting-crystallization of silver thiogallate by the statistical thermal analysis method

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Abstract The influence of heat treatment of a liquid phase on “melting-crystallization” processes of silver thiogallate ($AgGaS_2$) having chalcopyrite structure I $\bar{4}$2d, has been studied by the method of statistical thermal analysis (STA). It is shown that the melting temperature of solid phase (T_m) increases non-monotonic from 970 °C due to rise in the preliminary melt overheating, and T_m reaches asymptotically 1010 °C. The equilibrium melting-crystallization temperature (T_m^o) has been defined as 989.2 °C. It is also found an extreme dependence of the melt supercooling on its overheating. The two curves of irregular dependence of nucleation rate on melt supercooling have been plotted at different melt overheating.

Keywords Melting temperature · Nucleation · Supercooling · Thermal analysis · Silver thiogallate

Introduction

Crystallization of a liquid phase with a low nucleation rate and a high rate of crystal growth is widely used in most manufacturing processes of metallurgy, chemical and food industries, applied physics; in addition it is also a common geophysical process [1, 2]. The study of the preliminary melt or solid phase thermal treatment on kinetics and parameters of its crystallization, melting behavior, and other peculiarities of crystallization is of great interest for many applications in technique [3–7]. These effects are usually estimated over the melt supercooling which is random, stochastic [8]. Therefore, the most precise information on the nucleation kinetics may be provided by using of the statistical thermal analysis (STA) method [9, 10]. This method involves a sequential record of many curves of heating and cooling of one sample according to the given reproducible thermal regime. The technique of finding the dependence of a nucleation rate on melt supercooling over the data of a STA performed at a given cooling rate was developed in work [11]. Then, the STA method was used in studying the nucleation kinetics in melt of indium antimonide and germanium [12], lithium iodate [1, 8], proustite [1, 10], and tellurium [13].

This paper present the results of detailed statistical investigations of the melt supercoolings and the melting temperature (T_m) of silver thiogallate ($AgGaS_2$) performed by STA method and by plotting the kinetic curves of nucleation for some regimes of heat treatment of a liquid phase. The crystal of $AgGaS_2$ has non-centrosymmetric, non-polar structure of chalcopyrite type I $\bar{4}$2d, and high electro-optic coefficient and non-linear optical (NLO) susceptibility ($\sim$11.7 pm V^{-1}) [14]. The same symmetry and NLO properties have also some other sulfide and selenide crystals, and minerals: $CuFeS_2$, $CuGaS_2$, $CuInS_2$, $AgInS_2$, $AgGaSe_2$, and $CuGaSe_2$ [15]. So, the study of melting-crystallization processes of these compounds is interesting for applied physics, and mineralogy.

Experimental

Silver thiogallate was synthesized from the components by a two-temperature method at temperature sample $\sim$1050 °C, and at sulfur temperature $\sim$430–450 °C [13, 14]. All starting substances (Ag, Ga, S) had a high degree of purity with the total impurity content of 10^{-3} wt %. Sulfur was

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beforehand dehydrated by melting in a vacuum. The synthesis was performed in a sealed quartz ampoule, then this material underwent to unidirectional crystallization with evacuation of gases liberated during the synthesis. The light-yellow sample of substance of 1 cm^3 volume was sealed into the quartz ampoule at a vacuum of 10^{-6} mmHg. The free volume above sample was also $\sim$1 cm^3. In order to avoid a cracking of the ampoule with silver thiogallate, this ampoule was covered with pyrolytic graphite.

An automatic installation of STA enabled us to effect different thermal cycles in course of some months [13]. The accuracy of keeping the presented regimes and the accuracy of the recording of the whole system amounted to ±0.5 °C. For one cycle of the thermal analysis the sample is heated up to melting (T_m), the melt is kept in an overheated state at temperature T_g for time 20 min and then cooled down to temperature 790–910 °C that guarantees the complete melt solidification. After this the cycle repeats itself. The number of cycles was 20–50 in experiments on determination of an average supercooling and 50–150 at determination of the nucleation dependence on overcooling. The cooling rate ranged from 0.5 to 10 °C min^{-1}. The total number of all experimental cycles exceeded 1500, and the duration of total experimental series–10 months. The moment of the crystallization onset is well fixed on the curve of a thermal analysis (temperature T_c). The extrapolation of the crystallization peak temperature (T_p) into the melt zero supercooling gives the temperature of the equilibrium crystallization of the substance [1, 8].

The equilibrium melting temperature of silver thiogallate (T°_m) was 989.2 ± 0.5 °C after long homogenization of the ingot in the many STA cycles. The initial melting temperature (T_m) was 970 °C. At the beginning of this STA series an unexplainable drop in temperature by 4–6 °C was observed on the heating curves after the melting plateaux recording. According to literature data the melting point of silver thiogallate is 965 ± 2 [16], 965.5–991 [17], 970 [15, 18], 980 [19, 20], 995 [21–23], 997–998 [24, 25], 1004–1005 [26, 27], $\sim$1010 [28], and 1040 °C [14, 29]. In [28], a small peak was observed on the DTA curves near the melting temperature. It corresponds to 993° ± 2° and 970 °C according to the data of [27], but this peak vanishes in long STA cycles of our experiments.

Two groups of experiments have been carried out for the same $AgGaS_2$ sample. (1) The dependence of average supercooling on melt overheating, i.e., on the greatest temperature (T_g) of heating of a liquid phase was determined. In doing so the overheating was gradually increased to a certain limit after 20–50 thermal cycles at each the greatest cycle temperature. (2) In this way such group of experiments was repeated, but the greatest STA temperature was decreased in a sequence of thermal cycles. The silver thiogallate sample use, we also studied the influence of the cooling rate, keeping of the melt in an overheating state on the kinetic characteristics of the nucleation process.

Results

The dependence of average supercooling of silver thiogallate melt (each point is average of 20 events) has a clear temperature hysteresis with the intersection nodal point of both curves at 20 °C, Fig. 1. The average supercooling ranges from 14 to 65 °C, while the minimum supercooling is equal to 3–5 °C, and the maximum supercooling reached 70 °C. The influence of the lowest STA cycles temperature (790–910 °C) on the supercooling of the silver thiogallate melt has not been found out. Figure 2 shows the dependence of the melting temperature on the greatest temperature $AgGaS_2$ melt in previous thermal cycle (T_g). It is seen, that there are two branches of this hysteresis dependence corresponding to increasing T_m in thermal cycles (curve 1), or decreasing T_m (curve 2). So, the melting temperature of $AgGaS_2$ irregular increase from 970 to 999.4 °C at consecutive raising of the greatest temperature cycles T_g from 970 to 1120 °C. At $T_\mathrm{g} = 1150$ °C, the melting temperature reaches $\sim$1008 °C. Then the melting temperature monotonously decreases to 989.2 °C in the series of experiments with the temperature T_g decreases. With the decrease of this temperature from 1035 to 993 °C, the $AgGaS_2$ melting temperature ranges in a narrow interval from 990.3 to 989.2 °C (curve 2, Fig. 2).

Figure 3 shows the dependence of the $AgGaS_2$ peak crystallization temperatures (T_p) on the nucleation onset temperature T_c. It is seen that the peak temperature of crystallization grows with an increase T_c. But, there two branches of this dependence corresponding to two curves in Fig. 2. The curve 1 (Fig. 3) is smooth extension of curve 2 (Fig. 2), which corresponds the series of experiments with

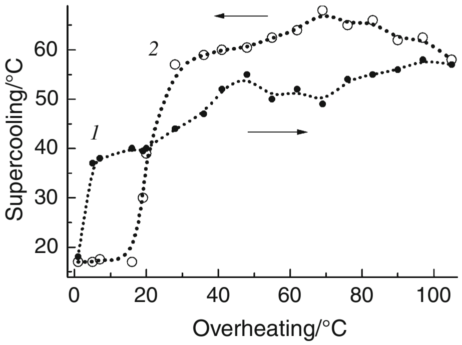

Fig. 1 Dependence of average values of the $AgGaS_2$ melt supercooling on the melt overheating: line *1*—at the movement towards an increase of overheating; line *2*—at the movement towards a decrease of overheating. For both lines: lower temperature thermal cycles 900 °C, overheating time 30 min, cooling rate 10 °C min^{-1}

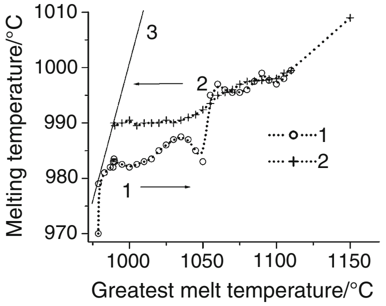

Fig. 2 The dependence of the melting temperature (T_m) on the greatest $AgGaS_2$ melt temperature in previous thermal cycle (T_g). Line *1*—at the movement towards an increase of T_g; line *2*—at the movement towards a decrease of T_g. Line *3* is that of equal temperatures

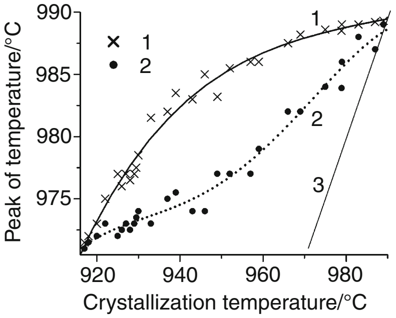

Fig. 3 The dependence of the peak crystallization temperature (T_p) on onset temperature of the $AgGaS_2$ melt crystallization (T_c). Line *1*—at the thermal regime of *curve 2*, Fig. 2. Line *2*—at the thermal regime of line *1*, Fig. 2. Line *3* is that of equal temperatures

the temperature T_g decreases. On the other side, curve 2, Fig. 3 obtains at the same series of experiments with the temperature T_g increases (curve 1, Fig. 2). So, the equilibrium temperature of melting-crystallization of $AgGaS_2$ is the point of intersection line 2, Fig. 2 with the line of equal temperatures (989.2 ± 0.5 °C).

Figure 4 shows the dependence of the nucleation rate of silver thiogallate on supercooling for preliminary overheating of the melt 5 °C (curve 1) and 70 °C (curve 2). The nucleation rate rises non-monotonously due to increase of melt supercooling. Sharp nucleation rate peaks are typical of melt crystallization of many other substances. In average, lg$J$ is proportional to the melt supercooling.

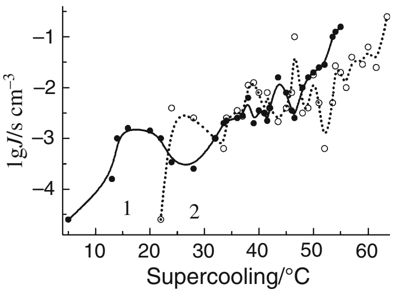

Fig. 4 Dependence of the nucleation rate J on supercooling (ΔT) of the $AgGaS_2$ melt for the preliminary melt overheating: line *1*—5 °C, line *2*—50 °C. For both lines: lower temperature thermal cycles—900 °C, overheating time is in minute, cooling rate is in °C min^{-1}

Discussion

So, the dependence of melting temperature of silver thiogallate on preliminary thermal condition of its synthesis, or on the greatest temperature of STA cycles is an unexpected result of this work. Early at STA investigation of melting-crystallization of other binary sulfide Ag_3AsS_3, the melting temperature was constantly, and equal 485 °C [1, 10]. Here, it is necessary note, that compound Ag_3AsS_3 has strong stoichiometric composition, while the limited solid solution $AgGaS_2$–Ga_2S_3 exists in system Ag_2S–Ga_2S_3 [27, 28]. The liquidus temperature of the (AgGa)–S system increases slightly from 980 to 1017 °C when pressure of sulfur achieves more 100 Pa [17, 30, 31]. The minimum melting temperature of light-yellow $AgGaS_2$ crystals equal 965.5 °C, while at $T_m = \sim 960$ °C the $AgGaS_2$ sample is dark-green [16]. The pure $AgGaS_2$ crystal having stoichiometric composition can be light-yellow. Because our experiment is carried out on the same sample, and free volume in ampoule is small, then there is other reason for explanation of this phenomenon. At normal pressure the ternary compound of $AgGaS_2$ has acentric non-polar tetragonal chalcopyrite structure I $\bar{4}$2d [31]. Both silver and gallium atoms have the same tetrahedral coordination, $Z = 4$. At pressure more than 4.5 GPa, the monoclinic $AgGaS_2$ phase has *Cm* space group of symmetry [32]. In solid phase of this compound, the distribution of Ag and Ga atoms between two metal sub-lattices can change at different temperatures and pressures [33]. Probably the change of solid $AgGaS_2$ microstructure can be a reason for non-constancy of melting temperature.

There is an empirical rule stating that the limit of supercooling is a fraction of the melting temperature, usually (0.2–0.33) T_m [1]. The principal feature of homogeneous crystallization is the strict reproducibility of results, the sharp boundary of metastability and no dependence of supercooling on overheating after the long keeping of a substance in a crystallized state near an equilibrium melting temperature as well as on the degree of substance purity. There are also other criteria based on a quantitative comparison of experimental data with theoretical concepts [1].

For silver thiogallate, theoretical estimation of the region of homogeneous nucleation equal 200–330 °C, while the real supercooling we observed do not exceed 70 °C. The absence of a sharp metastability boundary and the dependence of nucleation kinetics on the thermal prehistory of a liquid phase indicate that our experiments have been performed under the conditions of heterogeneous nucleation of melts. The melts of silver thiogallate appear to be crystallized according to the mechanism of heterogeneous nucleation on the walls of a quartz ampoule, or of a carbon coating. The supercooling of a melt of silver thiogallate (50–70 °C) achieved in our and in the other works are considerably less than those for homogeneous nucleation [1].

Probably, this is partly explained with the conducting substrate (graphite), which makes the nucleation more active [34]. In spite of a great dispersion of the achievable supercooling of melts and their dependence on numerous above-mentioned factors, the obtained average experimental data are reproducible, if it is possible to exactly reproduce the whole complex of thermal prehistory of a sample.

A well-defined monotonous increase in the melt supercooling with a rise of overheating within the limits of 0–30 °C has been found in the experiments on crystallization of melts of antimony [35, 36], germanium [1–12], indium antimonide [12], not so evident in the nucleation in melts of copper, iron, cobalt [36], while in the crystallization of melts of nickel, palladium, and gold the influence of overheating on supercooling has not been found [36]. Estimations show that all above-mentioned works have been performed in the region of melt supercooling with heterogeneous nucleation.

Conclusion

The above stated results of our statistical investigation of the nucleation kinetics in melts illustrate well the potentialities of the STA method used in crystallization process study. The principal new facts are as follows.

1. Varying the regimes of heat treatment of a liquid, one can achieve deeper melt supercooling of the especially pure substances in many STA cycles.

2. At analysis of all experimental facts on the kinetics of heterogeneous nucleation of especially pure substances, one should take into account energy barriers of nucleation and the phenomena happening at the boundary "melt-container" as well as the change in the structure of a liquid and new crystalline phase. So, these phenomena should be further studied by using reliable statistical methods of thermal and differential thermal analyses in wider temperature intervals of heating and cooling of the inorganic substances.

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