

PHYSICOCHEMICAL ANALYSIS
OF INORGANIC SYSTEMS

Crystallization Features
of Ternary Reversible Reciprocal Systems

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Abstract—Some features of the primary crystallization of phases in ternary reversible reciprocal system are considered and discussed. The diagonal join CdTe–GeSe of the CdTe + GeSe \rightleftharpoons CdSe + GeTe ternary reciprocal system is studied to show that the features in primary and secondary heating and cooling curves in such systems under fully equilibrium conditions are not reproduced upon consecutive heating and cooling sessions, because of the existence of different amounts of the reagents and the reaction products in the mixture; the temperatures of each transformation lie in a range. Those who experimentally investigate other ternary and more complex reversible reciprocal systems should take this fact into account.

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The experimental investigation of ternary reciprocal systems, although they are the simplest reciprocal systems, is in many cases complicated by exchange chemical reactions. About one thousand of ternary reciprocal systems have been investigated [1, 2], but the primary and secondary crystallization features in such systems are far from being fully understood.

The ternary systems can roughly be grouped into singular, irreversible reciprocal, and reversible reciprocal systems [3]. It was shown in [4] that primary and secondary crystallization along the stable join of a ternary reversible reciprocal system is nonequilibrium as a result of the partial exchange reaction between the salts of this join; the figurative point is displaced from the diagonal join into the ternary system. As a result of nonequilibrium crystallization, secondary separation along such a join does not occur at a constant temperature; the position of the secondary separation line is a function of the eutectic temperatures in the binary systems that bound the square of the reversible reciprocal system, of the eutectic temperature of the stable diagonal section, and the ternary eutectic temperatures. However, the details of primary crystallization in reversible reciprocal systems were not considered under fully equilibrium conditions ($\Delta G_T \approx 0$), where it is impossible to clearly recognize the stable pair among the components of the system [4]. Here we consider some features of primary crystallization in such ternary reversible reciprocal systems, because of various problems arising in the design of their phase diagrams. There is no quasi-binary diagonal join in such systems [3] since the Gibbs energy change in the exchange reaction is insignificant ($\Delta G_T \leq 10$ kJ/mol [2]). However, a stable

salt pair exists in some of such systems; this pair appears in the crystallization products of any mixture of the components.

Consider a ternary reciprocal system $AX + BY \rightleftharpoons AY + BX$ in which the Gibbs energy change from room temperature to 1500 K is near zero. The relation between ΔG_T and the equilibrium constant K_p is expressed through $\Delta G_T = -RT \ln K_p$. If $\Delta G_T = 0$, $\ln K_p$ is also zero, and $K_p = 1$. An equilibrium mixture under these conditions will contain all four components of the ternary reciprocal system. If the mole fraction of component BY in mixture $AX + BY$ is x and if the extent of the reaction between AX and BY is y , the concentrations of the four components in the reacted mixture may be written as

$$\{(1-x)AX + xBY\}_y + \{xAY + xBX + (1-2x)AX\}_{1-y} = 1. \quad (1)$$

Note that in our case $0 < x < 0.5$, since the $(1-x)AX + xBY$ and $xAX + (1-x)BY$ are equivalent writings. This is confirmed by the fact that a ternary reciprocal system may formally be considered as a system consisting of two ternary systems in which one boundary binary is common. For example, system $AX + BY \rightleftharpoons AY + BX$ (Fig. 1) may be treated as a system consisting of ternary systems AX – AY – BY and AX – BX – BY or AX – AY – BX and AY – BX – BY . In the former case, the common binary is diagonal AX – BY ; in the latter, it is diagonal AY – BX .

The extent of reaction y in an equilibrium mixture (i.e., at $\Delta G_T \approx 0$) can vary from 0 (no reaction) to 1

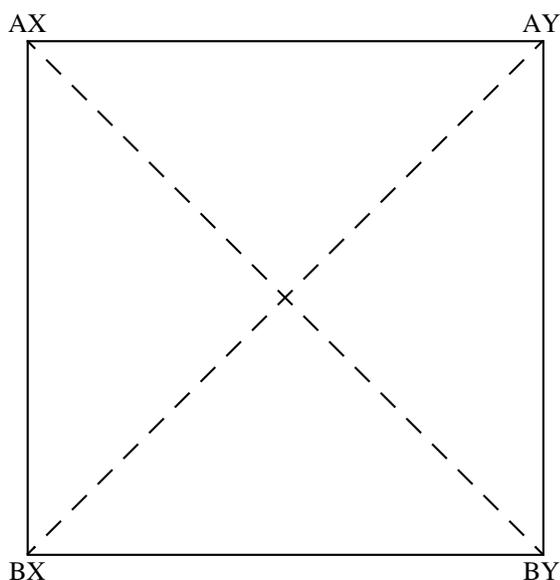


Fig. 1. Scheme of the diagonal joins in an $AX + BY \rightleftharpoons AY + BX$ ternary reversible reciprocal system.

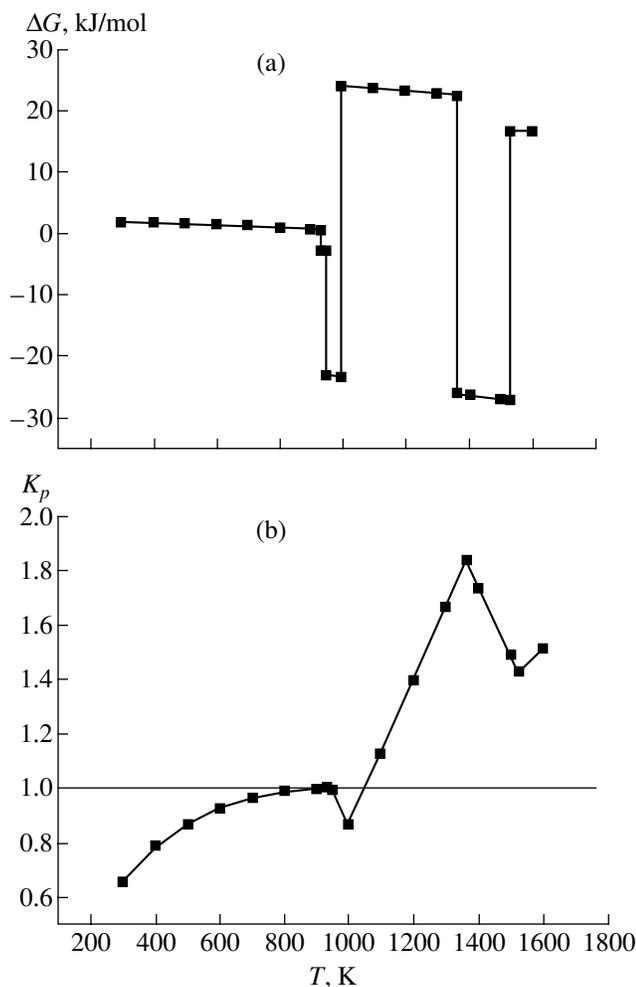


Fig. 2. Temperature plots for (a) the Gibbs free energy and (b) the equilibrium constant of the reaction $CdTe + GeSe \rightleftharpoons CdSe + GeTe$.

(complete reaction of the components); its particular value is a function of many parameters. Such parameters may be the shape of the ampoule in which the reaction is studied, the temperature gradient in the furnace, the location of separate phases of the terminal components and the reaction products, the heating or cooling rate, and the like. One easily finds from Eq. (1) that the concentrations of AX and BY in alloys can vary from 0 to x , the concentration of BY from x to 0, and the concentration of AX from $(1 - x)$ to $(1 - 2x)$ as the extent of reaction decreases from 1 to 0. For example, if $x = 0.3$, the mole fractions of the components in the equilibrium mixture are, depending on y , 0–0.3 for AY, 0–0.3 for BX, 0.3–0 for BY, and 0.7–0.4 for AX. An experimental investigation of the diagonal joins of such a reversible reciprocal ternary system can meet some difficulties, because the composition of the reacting mixture changes after each cooling session. Therefore, presumably, the DTA thermal features in the primary and secondary heating and cooling curves will not reproduce and the phase-transformation temperatures will be in a range. The micrographs of a sample will show different amounts of coexisting phases after each heating and cooling session.

Our experimental study of the $CdTe + GeSe \rightleftharpoons CdSe + GeTe$ ternary reciprocal system supports the above speculations. The Gibbs energy change in the specified reaction is plotted in Fig. 2a. The thermodynamic parameters of the components of the exchange chemical reaction used in the calculations are listed in Tables 1 and 2. The ΔG_T of this reaction has near-zero values over a wide range from room temperature to 900 K. Therefore, the equilibrium constants of the reaction approach unity (Fig. 2b). Thus, the $CdTe + GeSe \rightleftharpoons CdSe + GeTe$ ternary reciprocal system satisfies the requirements of this work for ternary reversible reciprocal systems, and its experimental investigation should confirm our hypotheses, advanced on the basis of the theoretical consideration of this type of system.

Differential thermal analysis (DTA), microstructure observation, and microhardness measurements are used to study the exchange reaction in the $CdTe + GeSe \rightleftharpoons CdSe + GeTe$ system along the diagonal join CdTe–GeSe. DTA is carried out on a Netzsch DTA 402 installation. Pt/Pt–Rh thermocouples provided an error of ± 2 K in absolute temperatures and ± 0.5 K in temperature differences. Spectral pure SiO_2 is used as a reference. The DTA samples are prepared by alloying the constituent elements directly in the DTA ampoule evacuated to 10^{-2} Pa in order to eliminate substance loss upon transfer. The purity of the reagents is 6N grade. To improve the accuracy of recording thermal events, the total weight of each sample is 0.5000 g. All the samples are synthesized and homogenized in identical schedules (the same exposure time at the maximal melt temperature and the same cooling rate from the synthesis to

ambient temperature). The heating and cooling rate in the DTA range from 20 to 2 K/min.

After DTA, the samples are used for microstructure observations and microhardness measurements. An MMR-4 metallurgical microscope allows for the observation of mechanically lapped and polished surfaces in reflected light. Microhardness is measured on a PMT-3 tester with the goal of phase identification.

The experiments confirm our expectations that the features in repeated heating and cooling DTA curves for a sample of the same composition would not repeat; rather, they lay in a temperature range (Fig. 3). The liquidus peak temperature increases upon repeated heating and cooling sessions. An exotherm at an above-liquidus temperature recorded during the melt cooling confirms the existence of the exchange interaction that was inferred from the thermodynamic calculations. This exotherm may be due to the crystallization of a nascent CdSe-based phase from the melt.

The incongruent melting of GeSe [14] has no significant influence on the phase diagram for the CdTe–GeSe diagonal join, because of the appreciable displacement of the eutectic point toward germanium monoselenide.

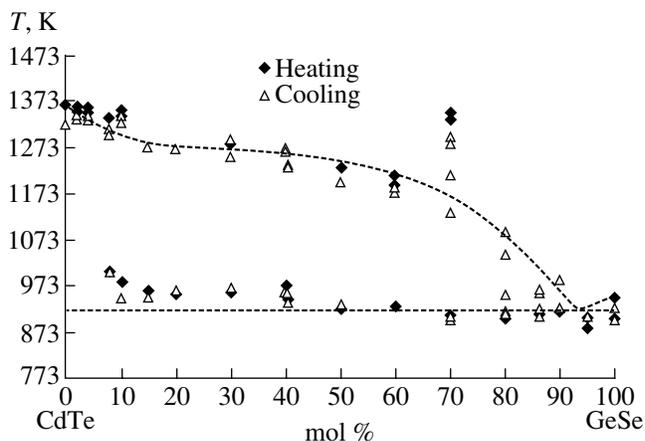


Fig. 3. Melting (crystallization) diagram for CdTe–GeSe alloys.

Since extensive solid solutions are formed at high temperatures in the CdTe–CdSe and GeTe–GeSe quasi-binary systems [14], only two main primary phases should crystallize as a result of the exchange chemical reaction in the $\text{CdTe} + \text{GeSe} \rightleftharpoons \text{CdSe} + \text{GeTe}$ system, namely, solid solutions $\text{CdSe}_x\text{Te}_{1-x}$ and $\text{GeSe}_y\text{Te}_{1-y}$.

Table 1. Thermodynamic parameters of the terminal components of the exchange chemical reaction $\text{CdTe} + \text{GeSe} \rightleftharpoons \text{CdSe} + \text{GeTe}$

Compound	$\Delta H_f^{\circ}, 298$, kJ/mol	Source	S_{298}° , J/(mol K)	Source	$T_{\text{ph. tr.}}$, K	Source	$\Delta H_{\text{ph. tr.}}$, kJ/mol	Source
CdSe	−144.30	[5]	84.70	[5]	1529	[6]	43.93	[7]
CdTe	−100.90	[8]	92.03	[8]	1365	[7]	48.53	[9]
GeSe	−82.43	[10]	79.08	[10]	934	[11]	3.34	[11]
GeTe	−37.24	[12]	88.91	[12]	951	[11]	20.08	[11]
					998	[7]	47.28	[12]

Table 2. Heat capacities of CdSe, CdTe, GeSe, and GeTe

Compound	$C_p = a + bT + cT^2 + d/T^2$, J/(mol K)				Temperature range, K	Source
	a	$b \times 10^3$	$c \times 10^5$	$d \times 10^{-5}$		
CdSe	48.46	5.87	−	−0.58	298–1529	[13]
	59.92				1529–2000	Calcd.
CdTe	49.33	8.62	−	−	298–1365	[7]
	63.60				1365–2000	Calcd.
GeSe	45.10	16.40	−	−	298–934	[12]
	45.10	16.40			934–951	Extrapol.
	63.20				951–2000	Calcd.
GeTe	48.12	12.55	−	−	298–998	[12]
	63.14				998–2000	Calcd.

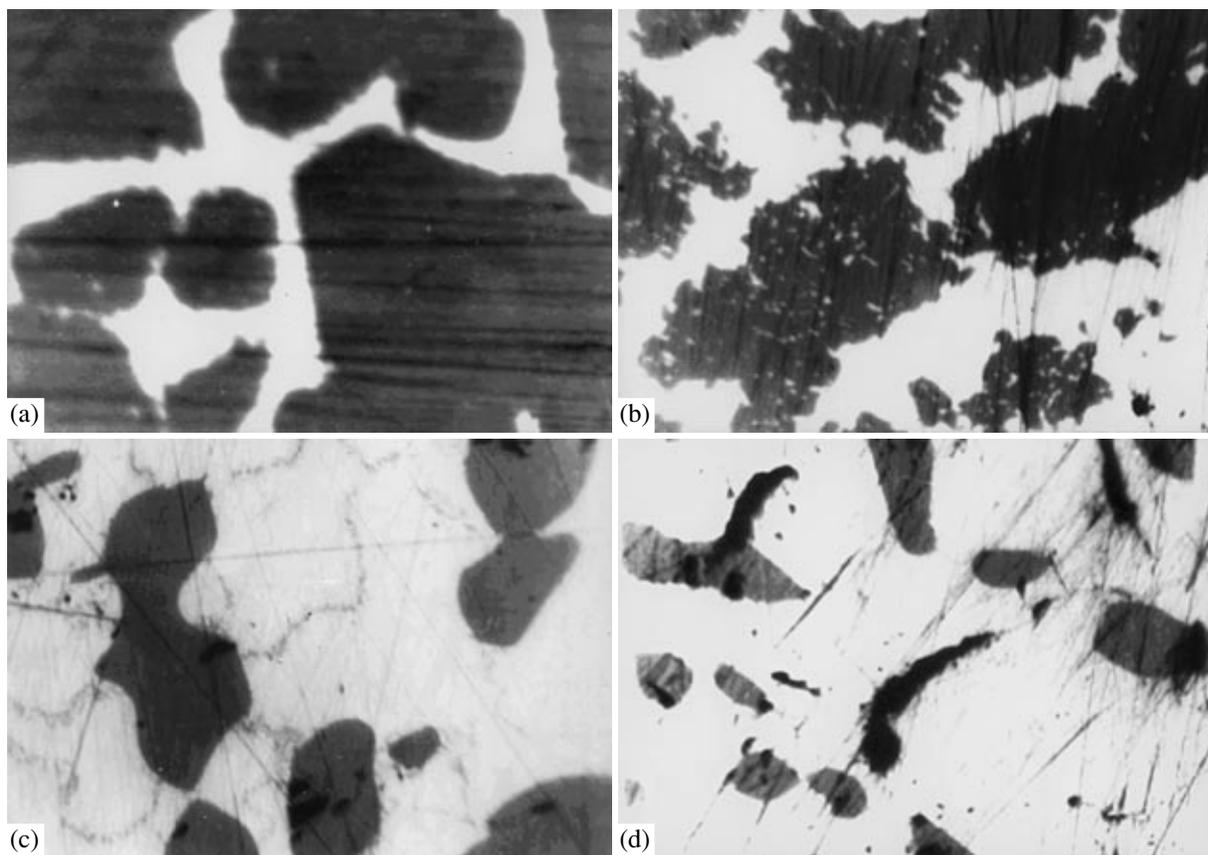


Fig. 4. Micrographs of CdTe–GeSe alloys containing (a) 15, (b) 40, (c) 70, and (d) 80 mol % GeSe. $\times 350$.

The microstructure observations (Fig. 4) clearly show only two phases in all micrographs. However, an insignificant amount of a component differing in shape from the CdTe-based phase is observed in the sample quenched after long-term (12-h) melt exposure at 1443 K (Fig. 4c); this may be a reaction product. A better equilibrated sample of the same composition (that has been cooled with a furnace) contains no microinclusions. The microhardness data support primary crystallization of two phases in the ternary system. The systematically increasing germanium monoselenide concentration increases the microhardness of the CdTe-based phase, and the increasing CdTe concentration increases the microhardness of the GeSe-based phase. These trends are characteristic of extensive solid solutions.

It is impossible to check, using microstructure observations, whether the ratio of the coexisting phases is different after each heating and cooling session, because of the sample preparation procedure used: the sample is removed from the quartz ampoule, lapped, photographed, again placed into an ampoule, evacuated, and again heated and cooled. Then, the microstructure observation is repeated. The results are irreproducible, since the same portion of a sample cannot be observed in repeated microstructure analysis. X-ray

diffraction shows only the CdTe- and GeSe-based phases in the samples annealed at 773 K.

In summary, having studied the diagonal join CdTe–GeSe of the CdTe + GeSe \rightleftharpoons CdSe + GeTe ternary reciprocal system, we show that the features in primary and secondary heating and cooling curves in such systems under fully equilibrium conditions are not reproduced upon consecutive heating and cooling sessions, because of the existence of different amounts of reagents and the reaction products in the mixture; the temperatures of each transformation lie in some range. Those who experimentally investigate other ternary and more complex reversible reciprocal systems should take this fact into account.

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