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Equilibrium Vapor Composition in the Pb–I_2 System

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Abstract—The equilibrium vapor composition in the Pb–I_2 system at temperatures from 400 to 2000 K and total pressures from 10^2 to 10^5 Pa was assessed by thermodynamic analysis. The results show that the dominant vapor species is PbI_2. PbI_2 dissociation is significant starting at 1000–1300 K, depending on the total pressure in the system.

INTRODUCTION

PbI_2 crystals are potentially attractive as materials for optical information recording systems, nonlinear optical devices, and x-ray and gamma detectors [1, 2]. The known techniques for melt growth of large PbI_2 crystals are incapable of ensuring the desired structural perfection of the crystals, which reflects on the engineering performance of PbI_2-based devices. Large, stoichiometric PbI_2 single crystals with a low dislocation density can be grown from the vapor phase in the presence of excess iodine [3]. This process, however, has not yet been studied in sufficient detail.

In this context, it is of interest to analyze the equilibrium vapor composition in a closed system. Information about the temperature-dependent compositions of the vapor and condensed phases helps to clarify the mechanism of mass transport in the growth system and optimize the growth procedure. By varying the process parameters, one can control the quality of the growing crystal.

EXPERIMENTAL

The equilibrium pressures of vapor species can be determined either experimentally or by thermodynamic calculations.

We used Knudsen cell mass spectrometric measurements to study the sublimation and thermal dissociation of PbI_2 in the temperature range 300–873 K. The mass spectra of saturated vapor over PbI_2 crystals showed the presence of PbI_2 molecules and minor amounts of iodine and lead.

CALCULATIONAL APPROACH

Although crystal growth from the vapor phase is a nonequilibrium process, it can be analyzed, to a reasonable approximation, with the use of equilibrium thermodynamics since knowledge of the equilibrium characteristics of the reactions involved makes it possible to draw a number of conclusions about the key features of the process as a whole, such as the reaction path, deviations from equilibrium, and the influence of individual reactions on the overall process.

To assess the vapor composition over PbI_2 in the temperature range 400–2000 K at total pressures of 10^2, 10^3, 10^4, and 10^5 Pa, we carried out thermodynamic analysis of the Pb–I_2 system. The vapor species included in our analysis were I, I_2, Pb, PbI, and PbI_2. The corresponding vapor-phase equilibria are

$$I_2(g) \rightleftharpoons 2I(g), \tag{1}$$

$$PbI_2(g) \rightleftharpoons PbI(g) + I(g), \tag{2}$$

$$PbI_2(g) \rightleftharpoons Pb(g) + I_2(g). \tag{3}$$

Depending on their melting and boiling points, the reactants may be in different states of aggregation, producing different vapor pressures. The equilibrium constants of independent reactions in the range 300–2000 K were calculated using the reported thermodynamic functions of the substances involved [4, 5] (table).

In terms of the partial pressures $p_1 = p(I)$, $p_2 = p(I_2)$, $p_3 = p(Pb)$, $p_4 = p(PbI)$, and $p_5 = p(PbI_2)$, the equilibrium constants for reactions (1)–(3) have the form

$$K_1 = p_1^2/p_2, \tag{4}$$

$$K_2 = p_1p_4/p_5, \tag{5}$$

$$K_3 = p_2p_3/p_5. \tag{6}$$

In addition,

$$p_1 + 2p_2 + p_4 + 2p_5 = 2(p_3 + p_4 + p_5) \tag{7}$$

(the amount of iodine atoms per unit volume is twice as

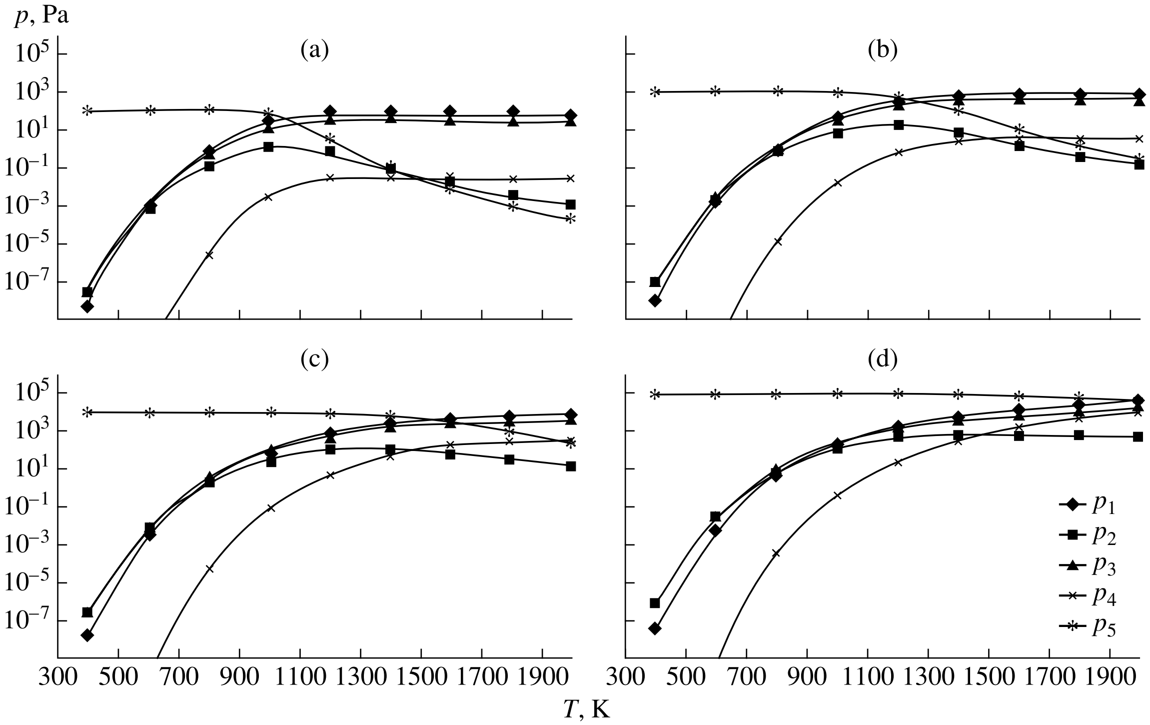

Fig. 1. Calculated temperature-dependent partial pressures in the Pb–I_2 system at total pressures of (a) 10^2, (b) 10^3, (c) 10^4, and (d) 10^5 Pa; p_1–p_5 have the same meaning as in text.

large as that of lead atoms),

$$p = p_1 + p_2 + p_4 + p_4 + p_5 \tag{8}$$

(Dalton Law).

Equilibrium constants of independent reactions in the Pb–I_2 system

T, K	K_1	K_2	K_3
300	4.2×10^{-25}	4.10×10^{-58}	1.20×10^{-31}
400	1.45×10^{-14}	4.10×10^{-40}	7.50×10^{-23}
500	2.8×10^{-11}	2.20×10^{-29}	7.20×10^{-18}
600	1.2×10^{-8}	2.86×10^{-22}	8.20×10^{-14}
700	1.02×10^{-6}	4.00×10^{-17}	6.50×10^{-11}
800	2.70×10^{-5}	1.40×10^{-13}	5.00×10^{-9}
900	3.60×10^{-4}	7.00×10^{-11}	1.70×10^{-7}
1000	4.20×10^{-3}	9.00×10^{-9}	2.40×10^{-6}
1100	1.50×10^{-2}	4.60×10^{-7}	1.90×10^{-5}
1200	6.20×10^{-2}	4.60×10^{-6}	6.20×10^{-5}
1300	0.20	3.06×10^{-5}	1.15×10^{-4}
1400	0.57	1.60×10^{-4}	2.00×10^{-4}
1500	1.39	6.50×10^{-4}	3.30×10^{-4}
1600	3.05	2.20×10^{-3}	5.03×10^{-6}
1700	6.09	6.70×10^{-3}	7.40×10^{-4}
1800	11.30	1.80×10^{-2}	1.04×10^{-3}
1900	19.70	4.20×10^{-2}	1.42×10^{-3}
2000	32.40	9.20×10^{-2}	1.90×10^{-3}

The system of nonlinear algebraic equations (4)–(8) can be reduced to an equation of the fourth degree in p_1:

$$\begin{aligned} &2p_1^4 + (K_1 + 3K_2)p_1^3 + (2K_1K_2 + 4K_1K_3)p_1^2 \\ &\quad + (3K_3K_1^2 - pK_1K_2)p_1 - 2K_3K_1^2p = 0. \end{aligned} \tag{9}$$

This equation was solved numerically. Next, using appropriate substitutions, we found p_2, p_3, p_4, and p_5. The calculated partial pressures of vapor species in the Pb–I_2 system at temperatures in the range 300–1700 K and different total pressures are displayed in Fig. 1.

DISCUSSION

The above results lead us to the following conclusions:

1. At total pressures from 10^2 to 10^5 Pa and temperatures from 300 to 1000 K, the dominant vapor species is PbI_2. Its pressure exceeds those of other vapor species by one to five orders of magnitude.

2. PbI_2 dissociation into I, I_2, Pb, and PbI is significant starting at 1000–1300 K, depending on the total pressure. The main dissociation products are I and Pb. The PbI vapor pressure rises with increasing temperature and total pressure but, in the range 300–1300 K, remains three to five orders of magnitude lower than the PbI_2 pressure. Only above 1500 K is the pressure of PbI vapor comparable to that of PbI_2, but the net iodide pressure (PbI + PbI_2) remains three to four orders of

magnitude lower than the pressure of the dissociation products (Pb, I, and I_2).

3. To a first approximation, the vapor-phase equilibrium in the Pb–I_2 system between 300 and 1000 K can be described by scheme (3).

Our experimental and calculation results on the equilibrium vapor composition in the Pb–I_2 system provide guidelines for choosing the conditions of PbI_2 growth from the vapor phase. Since the temperature of the growth zone should not exceed 685 K (melting point of PbI_2), and a temperature gradient of 100–400 K is typically sufficient for vapor transport growth, the highest temperature of the source zone is 1000–1100 K. At temperatures from 700 to 1100 K and total pressures from 10^3 to 10^5 Pa, the dominant vapor species in the Pb–I_2 system is PbI_2. The proportion of the dissociation products under these conditions does not exceed 1%. As PbI_2 slightly dissociates in the temperature range in question, which may lead to deposition of nonstoichiometric material, the process should be run at an iodine overpressure no lower than the dissociation pressure (10^3 Pa). The mechanism of mass transport in the growth system depends on the relationship between the total pressure and the difference in the vapor pressures in the source and growth zones.

Note that, in the growth procedure described in [3], the iodine overpressure is substantially higher than the pressure of PbI_2 dissociation at the temperatures of interest. At the same time, the growth duration is too long for practical applications. In this context, there is a need for theoretical analysis and experimental studies of the effects that the growth conditions and iodine overpressure have on the rate of PbI_2 transport and the morphology of the resulting crystals. Such information is crucial for optimizing the conditions of PbI_2 crystal growth. These issues will be addressed in subsequent communications.

REFERENCES

1. Indutnyi, I.Z., Kostyshin, M.T., and Kasyarum, O.P., *Fotostimulirovannye vzaimodeistviya v strukturakh metall–poluprovodnik* (Photoinduced Reactions in Metal–Semiconductor Structures), Kiev: Naukova Dumka, 1992.
2. Shieber, M., James, R.B., Lund, J.C., *et al.*, State of the Art of Wide-Band Gap Semiconductor Nuclear Radiation Detectors, *Nuovo Cimento Soc. Ital. Fis., A,* 1996, vol. 109, no. 9, pp. 1253–1260.
3. Rybak, V.M., Kalush, A.Z., and Logush, O.I., USSR Inventor's Certificate no. 1358487, *Byull. Izobret.,* 1987, no. 45, p. 44.
4. Ruzinov, L.P. and Gulyanitskii, B.S., *Ravnovesnye prevrashcheniya metallurgicheskikh reaktsii* (Equilibrium Transformations of Metallurgical Reactions), Moscow: Metallurgiya, 1975.
5. Rolsten, R.F., *Iodide Metals and Metal Iodides,* New York: Wiley, 1961. Translated under the title *Iodidnye metally i iodidy metallov,* Moscow: Metallurgiya, 1968.