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Thermodynamic Evaluation of Chemical Transport of VSe₂ and ZrSe₂ with Cl₂ and I₂ as Transporting Agents

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Abstract—To study chemical transport and refine synthetic routes, single crystals of vanadium and zirconium diselenides were grown by the chemical transport reaction method using I_2 and Cl_2 as transporting agents. The thermodynamic parameters of chemical transport have been evaluated, and the mass transfer direction in a growth ampoule has been determined. The phase composition of the samples has been examined by X-ray powder diffraction. Analysis of X-ray powder diffraction patterns of samples from the low- and high-temperature zones of the growth ampoule has confirmed the predictions based on thermodynamic calculations. With both transporting agents, $ZrSe_2$ transport occurs from the cold to the hot zone of the ampoule, while the direction of VSe₂ transport depends on the nature of the transporting agent. With I_2 as a transporting agent, transport occurs from the hot to the cold zone of the ampoule, while with Cl_2 , in the opposite mass transfer direction is observed. Microphotographs of the samples are consistent with thermodynamic and X-ray diffraction data. The results can be used to optimize the technology of producing layered transition metal dichalcogenides.

Keywords: TMDC, chemical transport reactions, vanadium diselenide, zirconium **DOI:** 10.1134/S0036023620090120

Layered transition metal dichalcogenides (TMDCs) are a group of binary compounds with a common characteristic structure and a very wide range of physicochemical properties. Layered TMDCs are distinguished by the variety of observed physical effects, catalytic activity, and extensive possibilities for obtaining nano- and intercalation materials based on them [1-3]. These qualities enable the use of TMDCs and materials based on them in rechargeable batteries [4-6] and for creating catalysts [7] and nanoscale electronic devices [8].

The structure of layered TMDCs consists of repeating layers separated by van der Waals gaps so that all covalent bonds in the structure lie within the same layer. In turn, the layers are linked with one another only through weak interatomic interactions. Each triple block comprises three atomic layers: two layers composed of chalcogen atoms and a layer of transition metal atoms located between them. Crystals of this structure belong to the structure type of CdI₂. The layered nature of TMDC crystals is responsible for the ease with which these compounds form intercalation compounds [9] and for their propensity to form thin films and 2D materials [10]. TMDC single crystals can replace graphene as substrates when creating heterostructures described in [11].

Versions of molecular beam epitaxy are currently a common method for producing nanoscale films of various materials [12]. This method allows one to control the thickness and stoichiometry of the synthesized layer with high accuracy, but is unsuitable for producing separate macroscopic single crystals. The main method for producing large single crystals of VSe₂ and ZrSe₂ is the chemical transport reaction (CTR) method [13, 14]. This method is based on a reversible reaction between a transported substance, in this case VSe₂ and ZrSe₂, and a transporting agent to give a gaseous transported form (for example, VI_4), the vapors of which move along the temperature gradient until the equilibrium is shifted in the opposite direction, which leads to the formation of XSe₂ crystals and the release of the transporting agent [15].

A common choice of transporting agent when using chemical transport reactions for the growth of TMDC single crystals is crystalline I_2 . The use of alternative transporting agents for the preparation of single crystals of Mo, Ta, V, and Zr dichalcogenides has been reported [16–18].

Unlike various ternary transition metal selenides, the thermodynamic parameters of which have been considered in detail [19], experimental data on the thermodynamic characteristics of layered V and Zr dichalcogenides are nearly absent in the literature.

Sustam	Weighed somple	T	Growth ter	Time h	
System	weighed sample, g	Transporting agent, ×10 × mol	$T_{\rm hot}$	$T_{\rm cold}$	Time, ii
VSe ₂	2.0	1.97 I ₂	850	800	48
VSe ₂	0.4	1.32 Cl ₂	850	800	48
ZrSe ₂	1.0	2.75 Cl ₂	915	850	48
ZrSe ₂	0.4	1.77 I ₂	850	800	48

Table 1. Parameters of growth of VSe₂ and ZrSe₂ crystals

This study deals with chemical transport processes in the MSe_2/I_2 and MSe_2/Cl_2 systems (M = V, Zr) in order to refine synthetic routes and conditions for growing single crystals of these compounds by the CTR method.

EXPERIMENTAL

Crystals of VSe₂ and ZrSe₂ were grown by the CTR method using Cl₂ and I₂ as a transporting agent. VSe₂ and ZrSe₂ crystals were produced from elements by annealing of a stoichiometric mixture of the starting elements in an evacuated ampoule. Then, the crystals together with the transporting agent source were loaded into a quartz ampoule, which was evacuated to a residual pressure of ~0.03 mbar and placed into a tubular furnace with a temperature gradient. The resulting crystals were characterized by X-ray diffraction on a Bruker D8 Advance diffractometer. Microphotographs of crystals were obtained using an MIM-7 microscope. The crystal growth conditions are presented in Table 1.

To avoid substance losses during evacuation and sealing of the growth ampoule, crystalline I_2 was introduced into it as a thin-walled Pyrex capillary, which was destroyed when the ampoule was heated to the growth temperature, releasing iodine vapor into the ampoule volume. Powders of VCl₃ and ZrCl₄ were introduced into the ampoule in a dry box under a nitrogen atmosphere. Upon heating in the growth ampoule, the transition metal halides VCl₃ and ZrCl₄ decompose to Cl₂ and VCl₂ or ZrCl₂, respectively.

Reactions (1)–(4) demonstrate the process of decomposition of a compound, a source of a transporting agent:

$$2\text{VCl}_3 \rightarrow \text{VCl}_4 + \text{VCl}_2,\tag{1}$$

$$2\text{VCl}_4 \rightarrow 2\text{VCl}_3 + \text{Cl}_2, \tag{2}$$

$$2ZrCl_4 \rightarrow 2ZrCl_3 + Cl_2, \qquad (3)$$

 $2ZrCl_3 \rightarrow ZrCl_4 + ZrCl_2. \tag{4}$

RESULTS AND DISCUSSION

On the basis of the data in [13, 15], we assume that, in the general case, the chemical transport process in

these systems can be described as follows: in the hightemperature zone of the furnace, a dichalcogenide reacts with a transporting agent, i.e. with halogen vapor, which leads to the formation of a gaseous tetrahalide. In the low-temperature region of the furnace, the halide reacts with selenium vapors to again form the XSe₂ dichalcogenide (X = V, Zr) and release the transporting agent (Cl₂ or I₂).

Reactions (5)–(8) approximately describe the course of the chemical transport in the MSe_2/CI_2 and MSe_2/I_2 systems (M = Zr, V).

$$ZrSe_{2(s)} + 2Cl_{2(g)} \leftrightarrow ZrCl_{4(g)} + Se_{2(g)},$$
(5)

$$ZrSe_{2(s)} + 2l_{2(g)} \leftrightarrow Zrl_{4(g)} + Se_{2(g)}, \tag{6}$$

$$VSe_{2(s)} + 2Cl_{2(g)} \leftrightarrow VCl_{4(g)} + Se_{2(g)}, \tag{7}$$

$$VSe_{2(s)} + 2l_{2(g)} \leftrightarrow Vl_{4(g)} + Se_{2(g)}.$$
 (8)

To get a more complete insight into the nature of the processes occurring during the synthesis and growth of $ZrSe_2$ and VSe_2 crystals by the CTR method, we evaluated the thermodynamic parameters of reactions (5)–(8) and the equilibrium constant in the temperature range from 298 to 1400 K.

In calculation of $\Delta_r G^0$ and K_p , it was assumed that $\Delta_f H$ of reactions in the range 298–1400 K is temperature independent. For VI₄ and ZrI₄, we used approxi-

mate values of the entropy of formation S_{298}^0 extrapolated using the known values for related halides. The need to introduce these assumptions is associated with the lack of reliable experimental data on the thermodynamic parameters of these substances in the literature [17–24]. The calculation results are presented in Table 2.

The temperature dependence of K_p is shown in Fig. 1. According to our estimates, the behavior of the equilibrium constant of reaction (8) with a change in temperature differs from that for reactions (5)–(7). In the range 300–1400 K, K_p decreases for reactions (5)–(7) and increases for reaction (8). In all the four cases, the rate of change in K_p decreases with increasing temperature.

The temperature dependence of the free Gibbs energy of reaction $\Delta_r G$ is shown in Fig. 2. Approximate calculations show that $\Delta_r G$ decreases with increasing

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System	$\Delta_r H_{298}^0$, kJ/mol	$\Delta_r S_{298}^0$, kJ/(mol K)	$\Delta_r G_{298}^0$, kJ/mol	$K_{p}^{(298)}$	$\Delta_r G_{1188}^0$, kJ/mol	$K_{p}^{(1188)}$	$\Delta_r G_{1123}^0$, kJ/mol	$K_{p}^{(1123)}$
ZrSe ₂ /Cl ₂	-414.3	-0.10	-382.31	1.17	-287.7	1.029	—	_
$ZrSe_2/I_2$	-41.4	0.18	-95.59	1.04	-257.7	1.026	—	—
VSe ₂ /Cl ₂	-259.9	0.28	-344.20	1.15	—	—	-606.6	1.06
VSe ₂ /I ₂	49.5	0.14	5.09	0.10	—	—	-117.9	1.01

 Table 2. Approximate thermodynamic parameters of CTR

temperature for reactions (5), (7), and (8). For reaction (6), $\Delta_r G$ increases and become positive at T = 3889.7 K. For reaction (8), $\Delta_r G_{298}^{\circ}$ is slightly >0, but $\Delta_r G$ decreases with increasing temperature.

The relationships between $\Delta_r G$, $\Delta_r H$, and $\Delta_r S$ make it possible to predict the behavior of the transport reaction in each particular case according to the rules deduced in [15]. These trends are presented in Table 3.

The observed experimental results coincide with the predicted course of the transport process. In the cases of $ZrSe_2/Cl_2$, $ZrSe_2/I_2$, and VSe_2/Cl_2 , crystal growth is observed in the high-temperature zone of the ampoule and insignificant formation of small crystals, in the low-temperature zone, which indicates the coexistence of several transfer mechanisms in the growth ampoule. In the case of $ZrSe_2$, the accumulation of impurity phases of various composition is observed in the low-temperature zone of the ampoule. In the case of VSe_2/I_2 , the formation of numerous large single crystals is observed in the low-temperature zone.







Fig. 2. Temperature dependence of $\Delta_r G$ of transport of (a) ZrSe₂ and (b) VSe₂.

The X-ray diffraction patterns of the samples are shown in Fig. 3. For vanadium diselenide, the use of both transporting agents leads to the formation of pure VSe_2 in the high- and low-temperature zones, which indicates the efficient operation of the transfer mechanisms. The differences in peak intensities are explained by the size of the crystals and the texture of the resulting material.

In the case of $ZrSe_2$, the X-ray diffraction pattern demonstrates the formation of $ZrSe_2$ and the lack of noticeable impurities in the high-temperature zone,

System	$\Delta_r S_{298}^0$	$\Delta_r H^0_{298}$	$\Delta_r G_{298}^0$	Possibility of the reaction	Transport direction
ZrSe ₂ /Cl ₂	<0	<0	<0	Limited from above by T	$T_{\rm cold} \rightarrow T_{\rm hot}$
ZrSe ₂ /I ₂	>0	<0	<0	Possible	$T_{\rm cold} \rightarrow T_{\rm hot}$
VSe ₂ /Cl ₂	>0	<0	<0	Possible	$T_{\rm cold} \rightarrow T_{\rm hot}$
VSe ₂ /I ₂	>0	>0	>0	Limited from below by T	$T_{\rm hot} \rightarrow T_{\rm cold}$

Table 3. Evaluation of the possibility of the transport reaction and transfer direction



Fig. 3. X-ray diffraction patterns of (a) VSe₂ samples formed in the high-temperature zone of an ampoule with (*I*) Cl₂ and (*2*) I₂ and in the low-temperature zone with (*3*) Cl₂ and (*4*) I₂ (*a*-characteristic peaks of VSe₂, PDF 01-074-1411); and (b) ZrSe₂ samples formed in the high-temperature zone of an ampoule with (*I*) Cl₂ and (*2*) I₂ and in the low-temperature zone of an ampoule with (*I*) Cl₂ and (*2*) I₂ and in the low-temperature zone of an ampoule with (*I*) Cl₂ and (*2*) I₂ and in the low-temperature zone of an ampoule with (*I*) Cl₂ and (*2*) I₂ and in the low-temperature zone of an ampoule with (*I*) Cl₂ and (*I*) Cl₂ and (*I*) Cl₂ (*a*-ZrSe₂ (PDF 03-065-3376), *b*-ZrSe₃ (PDF 00-036-1338), *c*-ZrCl₂ (PDF 01-072-1904), *d*-Zr₄Se₃ (PDF 00-015-0221), *e*-Se (PDF 00-027-0603)).

while $ZrSe_3$ and other impurities are accumulated in the low-temperature zone, which confirms the hypothesis that chemical transport occurs towards the hotter zone.

The micrographs of the samples from the high- and low-temperature zones of the growth ampoule clearly show a layered structure of the synthesized crystals (Figs. 4d and 4f). The presence of characteristic angles of 120° demonstrates the crystals have a hexagonal structure. In Fig. 4g, a crystal of ZrSe₃, which is the major impurity phase in this sample, can be seen.

CONCLUSIONS

The chemical transport of layered dichalcogenides VSe_2 and $ZrSe_2$ with the participation of I_2 and Cl_2 as a transporting agent is considered.

The CTR method with I_2 and Cl_2 as transporting agents afforded samples of VSe₂ and ZrSe₂.

A thermodynamic evaluation of the direction and possibility of the process at different temperatures predicts that the transport should proceed from the low-temperature zone to the high-temperature zone of the ampoule in the case of VSe_2/Cl_2 and in the case of



Fig. 4. Microphotographs of the substance removed from the high-temperature (hot) and low-temperature (cold) zones of growth ampoules. VSe_2/Cl_2 : (a) cold, (b) hot; VSe_2/I_2 : (c) cold, (d) hot: $ZrSe_2/Cl_2$: (e) cold, (f) hot; $ZrSe_2/I_2$: (g) cold, (h) hot. All images were obtained at the same magnification.

ZrSe₂, regardless of the nature of the transporting agent. In the case of VSe_2/I_2 , the transport should proceed in the direction of the low-temperature zone. Studies of the phase composition of the samples from the high- and low-temperature zones of growth ampoules confirm this assumption. The thermodynamic parameters of chemical transport processes have been evaluated, but taking into account the assumptions made in the calculations, the values of these quantities should be considered approximate

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

REFERENCES

- Q. H. Wang, K. Kalantar-Zadeh, A. Kis, et al., Nat. Nanotech. 7, 699 (2012). https://doi.org/10.1038/nnano.2012.193
- S. Das, J. A. Robinson, M. Dubey, et al., Annu. Rev. Mater. Res. 45, 1 (2015). https://doi.org/10.1146/annurev-matsci-070214-021034
- C. N. R. Rao, H. S. S. Ramakrishna Matte, and U. Maitra, Angew. Chem., Int. Ed. Engl. 9, 13162 (2013). https://doi.org/10.1002/anie.201301548

- Y. Y. Lee, G. O. Park, Y. S. Choi, et al., RSC Adv. 6, 14253 (2016). https://doi.org/10.1039/C5RA19799F
- Y. Onuki, R. Inada, S. Tanuma, S. Yamanaka, et al., Solid State Ionics 8, 141 (1983). https://doi.org/10.1016/0167-2738(83)90075-9
- A. H. Thompson, J. C. Scanlon, and C. R. Symon, Solid State Ionics 1, 47 (1980). https://doi.org/10.1016/0167-2738(80)90021-1
- 7. H. Li, X. Jia, Q. Zhang, and X. Wang, Chem 7, 1510 (2018).
- https://doi.org/10.1016/j.chempr.2018.03.012 8. T. Roy, M. Tosun, J. S. Kang, et al., ACS Nano **8**, 6259
- I. Koy, M. Tosun, J. S. Kang, et al., ACS Nano 8, 6259 (2014). https://doi.org/10.1021/nn501723y
- J. Rouxel, Physica B+C 99, 3 (1980). https://doi.org/10.1016/0378-4363(80)90203-X
- Zh. Zhang, P. Yang, M. Hong, et al., Nanotechnology 30, 182002 (2019). https://doi.org/10.1088/1361-6528/aaff19
- E. Yu. Buslaeva, S. V. Kraevskii, Yu. A. Groshkova, et al., Russ. J. Inorg. Chem. 65, 5 (2020). https://doi.org/10.1134/S0036023620010040
- A. V. Kochura, S. F. Marenkin, et al., Russ. J. Inorg. Chem. 63, 1087 (2018). https://doi.org/10.1134/S0036023618090139
- O. Tsukio, N. Hideaki, N. Mitsuoki, and I. Motohiko, J. Less-Common Met. 77, 185 (1981). https://doi.org/10.1016/0022-5088(81)90169-7
- M. J. Mleczko, C. Zhang, H. R. Lee, et al., Sci. Adv. 3, e1700481 (2017). https://doi.org/10.1126/sciadv.1700481
- 15. H. Schefer, *Chemical Transport Reactions* (Academic Press, New York, 1964; Mir, Moscow, 1964).

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- A. Ubaldini, J. Jacimovic, N. Ubrig, and E. Giannini, Cryst. Growth Des. 13, 4453 (2013). https://doi.org/10.1021/cg400953e
- K. S. Nikonov, M. N. Brekhovskikh, A. V. Egorysheva, et al., Inorg. Mater. 53, 1126 (2017). https://doi.org/10.1134/S0020168517110061
- K. S. Nikonov, M. N. Brekhovskikh, T. K. Menshchikova, and V. A. Fedorov, Inorg. Mater. 55, 898 (2019). https://doi.org/10.1134/S0020168519090097
- M. B. Babanly, L. F. Mashadiyeva, D. M. Babanly, et al., Russ. J. Inorg. Chem. 64, 1649 (2019). https://doi.org/10.1134/S0036023619130035
- A. V. Blinder, A. S. Bolgar, and Zh. A. Trofimova, Powder Metall. Met. Ceram. 32, 234 (1993). https://doi.org/10.1007/BF00559756

- 21. K. C. Mills, *Thermodynamic Data for Inorganic Sulphides, Selenides and Tellurides* (Butterworths, London, 1974).
- 22. *Thermal Constants of Substances*, Ed. by V. P. Glushko (VINITI, Moscow, 1965–1982), Iss. 1–10, [in Russian].
- F. K. McTaggart and A. D. Wadsley, Aust. J. Chem. 11, 445 (1958). https://doi.org/10.1071/CH9580445
- 24. J. G. Hooley, Preparation and Crystal Growth of Materials with Layered Structures, Ed. by R. M. A. Lieth (Springer, Dordrecht, 1977). https://doi.org/10.1007/978-94-017-2750-1

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