Distribution Coefficients of Impurities in Cadmium Fluoride

S. P. Ivanov, I. I. Buchinskaya, and P. P. Fedorov

Shubnikov Institute of Crystallography, Russian Academy of Sciences, Leninskii pr. 59, Moscow, 117333 Russia Received April 29, 1999; in final form, December 10, 1999

Abstract—Experimental data on the liquidus curve in cadmium fluoride–metal fluoride systems were used to calculate the distribution coefficients of di- and trivalent impurities in CdF_2 . A similar method was proposed for calculating the distribution coefficient from solidus data. It was shown that the variations of the calculated distribution coefficients with the ionic radii of M^{2+} and R^{3+} are well fitted by Gaussians. Phase relations in the CdF_2 -rich part of the CdF_2 -InF₃ system were studied by differential thermal analysis and x-ray diffraction.

INTRODUCTION

The interesting properties of cadmium fluoride and related materials make them potentially attractive for many technological applications. CdF_2 crystals are transparent in the visible and IR ranges and, under certain conditions, exhibit semiconducting behavior [1, 2]. CdF_2 is used as a constituent of IR-transparent fluoride glasses, fluorine-ion-conducting solid electrolyte, material for laser arrays and IR detectors, and medium for optical information processing systems [3–7]. In view of this, the ability to grow high-purity CdF_2 crystals with controlled dopant distribution is of immense practical importance.

Precise knowledge of impurity distribution coefficients in CdF_2 is critical for devising purification procedures and predicting impurity profiles in melt-grown crystals. The distribution coefficients of rare-earth fluorides extrapolated to infinite dilution were evaluated in [8] with the use of the experimental data obtained by Sattarova [9]. In this work, we calculate the distribution coefficients of di- and trivalent impurities in CdF_2 by the method proposed in [8], using earlier data on the liquidus curve in cadmium fluoride-metal fluoride systems [10–16]. We also consider a method for evaluating the distribution coefficient from data on the solidus curve.

Although CdF₂:In is a candidate material for optical information processing applications [7] and neutrino detection [17], the CdF₂-InF₃ system has not yet been studied. For this reason, we investigated a portion of the phase diagram of this system.

INVESTIGATION OF THE CdF₂-InF₃ SYSTEM

The CdF_2 -InF₃ system was studied by differential thermal analysis (DTA) and x-ray diffraction (XRD). The starting materials used were reagent-grade CdF₂,

additionally melted in a fluorinating atmosphere resulting from pyrolysis of polytetrafluoroethylene and purified to a light yellow coloration by directional solidification, and powder InF_3 prepared by fluorinating indium oxide in flowing HF at 400°C. The InF_3 powder was stored in a desiccator over P_2O_5 all the time before synthesis. The XRD data for the starting materials agreed with those given in the JCPDS Powder Diffraction File. CdF₂ had the fluorite structure (sp. gr. *Fm3m*) with a = 5.388 Å. InF_3 had a hexagonal unit cell (trigonally distorted ReO₃ type) with a = 5.401 Å and c =14.40 Å.

In DTA characterization, we used a special unit intended for studies of fluorides.¹ The temperature was monitored with W–5% Re/W–20% Re thermocouples calibrated against the melting points of Pb, Sn, NaCl, LiF, NaF, and YF₃. DTA scans were carried out under a helium atmosphere in an open thin-wall graphite crucible at a heating/cooling rate of 30–50°C/min. The solidus and liquidus temperatures were determined as the initial peak temperatures in the heating and cooling curves, respectively.

Powder XRD patterns were recorded on an AFV-202E Toshiba diffractometer (Ni-filtered CuK_{α} radiation).

 CdF_2 and InF_3 were found to form a eutectic, with a broad range of CdF_2 -based solid solutions (Fig. 1). The eutectic temperature is $800 \pm 5^{\circ}C$. We failed to study phase relations in the InF_3 -rich part of the system because of the high volatility of InF_3 .

After DTA scans, the samples containing $5-15 \mod \%$ InF₃ were transparent, light yellow, characteristic of CdF₂. The samples containing 20–30 mol % InF₃ were white and opaque. The XRD patterns of these latter

¹ Shubnikov Institute of Crystallography, Russian Academy of Sciences.

showed the presence of InF_3 . These results indicate that the maximum solubility of InF_3 in CdF_2 is 19 ± 2 mol %, in reasonable agreement with the prediction in [1] and the reported data on the limit of the solid solutions of InF_3 in CdF_2 prepared by solid-state reaction at 750°C [18].

CALCULATION OF DISTRIBUTION COEFFICIENTS

Distribution coefficients were calculated by the method proposed in [8], which relies on the van't Hoff's limit equation,

$$\lim_{x \to 0} \frac{dT}{dx^L} = \frac{RT_0^2}{\Delta H}(k-1), \tag{1}$$

where T_0 and ΔH are, respectively, the melting point and heat of melting of the host, x^L is the mole fraction of the impurity, and T is the liquidus temperature at x^L .

Over a broad composition range, experimental data on the liquidus curve were represented by a polynomial,

$$T = a_0 + a_1 x + a_2 x^2 + \dots = \sum_{i=1}^n a_i x^i, \qquad (2)$$

where

$$\left. \frac{dT}{dx^L} \right|_{x=0} = a_1. \tag{3}$$

In our least squares calculations, we used polynomials of degree two or three, and the melting point was fixed at $T_0 = 1348$ K. The liquidus curve was fitted in the range from 0 to 20–30 mol % impurity. The heat of melting of cadmium fluoride was taken to be 22572 J/mol (5400 cal/mol) [19].

For solid-solution systems, k can be calculated by a similar procedure, using data on the solidus curve. Since

$$\frac{dT}{dx^L} = k \frac{dT}{dx^S},\tag{4}$$

equation (1) takes the form

$$\lim_{x \to 0} \frac{dT}{dx^{s}} = \frac{RT_{0}^{2}}{k\Delta H}(k-1).$$
 (5)

Data on the solidus curve are also represented with a polynomial, and then the distribution coefficient is calculated as described above.

RESULTS AND DISCUSSION

The results on the distribution coefficients of various impurities in cadmium fluoride are summarized in Table 1. In analyzing these data, we used Shannon's

INORGANIC MATERIALS Vol. 36 No. 4 2000



Fig. 1. Partial phase diagram of the CdF₂-InF₃ system: (1) DTA data, (2) limit of solid solutions according to Lagassie *et al.* [18]; $F = Cd_{1-x}In_xF_{2+x}$ fluorite solid solution, L = melt.

eightfold-coordinated ionic radii [20]. In evaluating the ionic radii of Ni^{2+} and Ga^{3+} , we took into account the data reported in [21].

Figures 2-4 show the distribution coefficients of metal di- and trifluorides in CdF₂ as functions of the ionic radius of M²⁺, that of R³⁺, and the $\Delta r/R$ ratio, where Δr is the difference in ionic radius between the metal and cadmium, and $R = a \sqrt{3}/4$ is the cation-anion distance in CdF₂ (a = 5.388 Å is the lattice parameter of CdF₂).

The curves are similar in shape and are well fitted by Gaussians:

$$k = 1.30 \exp[-35.72(r - 1.216)^{2}], \qquad (6)$$

$$k = 1.26 \exp[-52.38(\Delta r/R)^{2}]$$
(7)

for MF₂ and

$$k = 1.24 \exp[-62.21(r-1.16)^2],$$
 (8)

$$k = 1.24 \exp[-102.86((\Delta r/R) + 0.059)^2]$$
 (9)

for MF₃.

By using the $\Delta r/R$ ratio, as proposed in [22], we obtain nondimensional coefficients.



Fig. 2. Distribution coefficient of MF_2 in melt-grown CdF_2 as a function of the ionic radius of M^{2+} . The curve represents a fit with equation (6).

For a particular impurity, the difference in the distribution coefficients derived from liquidus and solidus data is no greater than 10%. In particular, we find for $InF_3 k = 0.34$ from liquidus data and 0.33 from solidus data. When using the liquidus data derived from cooling curves for the CdF_2 -PbF₂ system [16], we obtained a negative k, which is physically meaningless, while the calculations from solidus data yielded a reasonable value, given in Table 1 (the other k values given in Table 1 were extracted from liquidus data). This is likely to indicate that, at the compositions studied, CdF_2 -PbF₂ melts supercool significantly, as supported by the data on the Bridgman growth of CdF_2 :Pb²⁺ crystals.

From solidus data for the CdF_2 -InF₃ system, we obtained k = 0.33, in good agreement (±10%) with the value extracted from liquidus data (Table 1) and the one



Fig. 3. Distribution coefficient of RF_3 in melt-grown CdF_2 as a function of the ionic radius of R^{3+} . The curve represents a fit with equation (8).

evaluated directly from phase-diagram data as $k = x^{S}/x^{L} = 0.34$.

Consider now our results in terms of isomorphism energetics [22]. According to the Termond–Strathers equation, in the case of an infinitely low impurity concentration, we have

$$\ln k_i = \frac{\Delta H_{\rm m}}{R} \left(\frac{1}{T_0} - \frac{1}{T_{\rm m}}\right) - \frac{\Delta G_i}{RT},\tag{10}$$

where $T_{\rm m}$ and $\Delta H_{\rm m}$ refer to the impurity, T_0 is the melting point of the host, and $\Delta \overline{G}_i$ is the difference in the partial molar Gibbs energies of solution of the impurity in the melt and crystal. This equation can be rewritten

М	r, Å	k	М	r, Å	k	М	r, Å	k
Ni	[0.99]	0.22	Ba	1.56	[0.05]	Y	1.159	1.38*
Mg	1.03	0.39	Ga	[0.785]	[0.05]	Dy	1.167	1.24*
Zn	1.04	0.39	In	1.06	0.34	Tb	1.18	1.05*
Co	1.04	0.41	Sc	1.01	0.34*	Gđ	1.198	0.95*
Mn	1.10	0.85	Lu	1.117	1.22*	Sm	1.219	0.91*
Cd	1.24	1.00	Yb	1.125	1.17*	Nb	1.249	0.77*
Ca	1.26	1.50	Tm	1.134	1.24*	Pr	1.266	0.74*
Sr	1.40	0.40	Er	1.144	1.31*	Ce	1.183	0.79*
Pb	1.43	0.17	Но	1.155	1.21*	La	1.30	0.28*

Table 1. Calculated distribution coefficients of metal di- and trifluorides in melt-grown CdF₂

* Earlier data [8].



Fig. 4. Distribution coefficients of (1) MF₂ and (2) RF₃ as functions of $\Delta r/R$. The curves show fits with equations (7) and (9).

in the form

$$k = k^0 \exp[-\Delta \overline{G}_i / (RT)], \qquad (11)$$

where

$$\ln k^0 = \frac{\Delta H_{\rm m}}{R} \left(\frac{1}{T_0} - \frac{1}{T_{\rm m}} \right).$$

Thus, each impurity must be characterized by its own k^0 value. In calculating k^0 , it is necessary to take into account that T_m and ΔH_m refer to that form of the impurity which has the same crystal structure as the host. This condition, not taken into account in [23], is fulfilled only for MF₂ with the fluorite structure (M = Ca, Sr, Ba, Pb). The results obtained for these compounds, using reference thermochemical data [19] and $T_0 = 1348$ K, are displayed in Table 2.

For difluorides with the rutile structure and trifluorides, substitution of the actual $T_{\rm m}$ and $\Delta H_{\rm m}$ values into (11) makes no sense since these compounds differ in structure type from CdF₂. It can be stated with assurance that the melting points and heats of melting of hypothetical fluorite forms of these compounds are substantially lower than those of the actual, rutile forms. For MnF₂, this issue was discussed in detail earlier [15].

Table 2. Thermochemical data and calculated k^0 for MF₂

¹ m, K	$\Delta H_{\rm m}$, KJ/mol	Ink ^o	k ⁰
1691	30.1	0.545	1.72
1741	29.7	0.598	1.82
1627	20.9	0.320	1.38
1098	12.55	-0.255	0.78
•	1691 1741 1627 1098	1691 30.1 1741 29.7 1627 20.9 1098 12.55	1691 30.1 0.545 1741 29.7 0.598 1627 20.9 0.320 1098 12.55 -0.255

The data in Table 2 demonstrates that k^0 does depend on the nature of the impurity, which introduces "noise" into the best-fit equation (7). Least squares fitting for the MF₂-CdF₂ systems yields $k^0 = 1.26$, which corresponds to the mean effective values $T_m = 1500$ K and $\Delta H_m = 25.5$ kJ/mol or $T_m = 1000$ K and $\Delta H_m =$ 7.25 kJ/mol.

There are no grounds to believe that $k^0 = 1$ in the general case, as suggested by Urusov [24]. In the case of isovalent isomorphism, the $\Delta \overline{G}_i \sim (\Delta r/R)^2$ correlation, following from (7) and (9), is in accordance with experimental data (see, e.g., [25]) and is associated with the effect of size factor on the mixing enthalpy.

The results obtained in the RF_3 -CdF₂ systems are in line with the conclusion that the optimum situation for heterovalent isomorphism with a variable number of ions in the unit cell is when the host and impurity cations differ in ionic radius [26, 27].

CONCLUSION

Phase relations in the CdF₂-rich part of the CdF₂-InF₃ system were studied, and Cd_{1-x}In_xF_{2+x} fluorite solid solutions were shown to exist for $x \le 0.19 \pm 0.02$.

The distribution coefficients of di- and trivalent impurities in melt-grown CdF_2 were calculated by a modified cryoscopy method from phase-diagram data.

The variations of the calculated distribution coefficients with the ionic radius and size factor $\Delta r/R$ (where R is the cation-anion distance in CdF₂) are well fitted by Gaussians.

REFERENCES

- Ryskin, A.I. and Fedorov, P.P., Donor Impurities and DX Centers in the Ionic Semiconductor CdF₂, *Fiz. Tverd. Tela* (S.-Peterburg), 1997, vol. 39, no. 6, pp. 1050–1055.
- Skorobogatov, B.S., Dubovik, M.F., Azarov, V.V., and Kol'per, L.B., Electroluminescent and Semiconducting Behavior of Rare-Earth-Doped CdF₂ Crystals, *Opt. Spektrosk.*, 1967, vol. 22, no. 6, pp. 931–933.
- Matecki, M., Poulain, M., and Poulain, M., Verres aux halogénures de cadmium: 1. Verres fluorés, *Mater. Res. Bull.*, 1982, vol. 17, pp. 1275–1281.
- Sorokin, N.I., Fedorov, P.P., Ivanov-Shits, A.K., and Sobolev, B.P., Fluorine Ionic Conductivity of CdF₂-Based Fluorite Solid-Solution Crystals, *Fiz. Tverd. Tela* (Leningrad), 1988, vol. 30, no. 5, pp. 1537–1539.
- Kaminskii, A.A., Kurbanov, K., Sarkisov, S.E., et al., Stimulated Emission of Nd³⁺ Ions in Non-Stoichiometric Cd_{1-x}Ce_xF_{2-x} and Cd_{1-x}Nd_xF_{2+x} Fluorides, *Phys. Status Solidi A*, 1985, vol. 90, pp. 55–60.
- Ryskin, A.I., Shcheulin, A.S., Miloglyadov, E.V., et al., Mechanisms of Writing and Decay of Holografic Gratings in Semiconducting CdF₂:Ga, J. Appl. Phys., 1998, vol. 83, no. 4, pp. 2215–2221.

- Ryskin, A.I., Shcheulin, A.S., Koziarska, B., et al., CdF₂:In: A Novel Material for Optically Written Storage of Information, *Appl. Phys. Lett.*, 1996, vol. 67, no. 1, pp. 31–33.
- Fedorov, P.P., Turkina, T.M., Lyamina, O.I., et al., Evaluation of the Impurity Distribution Coefficient from the Liquidus Curve in MF₂-RF₃ Systems, Vysokochist. Veshchestva, 1990, no. 6, pp. 67–72.
- 9. Sattarova, M.A., Phase-Diagram Studies of Systems of Cadmium Fluoride with Rare-Earth Trifluorides, *Cand. Sci. (Chem.) Dissertation*, Dushanbe, 1987.
- De Kozak, A., Les systèmes CrF₃-CdF₂ et CrF₃-PbF₂, C. R. Seances Acad. Sci., Ser. C, 1969, vol. 268, pp. 2184-2187.
- De Kosak, A., Samouel, M., and Chretien, A., Miscibilité cristalline des fluorures de calcium, de strontium et de plomb dans le fluorure de cadmium. Fluorure double Cd₂BaF₆, *Rev. Chim. Miner.*, 1971, vol. 8, pp. 805–811.
- Samouel, M. and de Kosak, A., Étude comparative des systèmes formés par CdF₂ et les fluorures des éléments alcalino-terreux, *Rev. Chim. Miner.*, 1972, vol. 9, pp. 815–819.
- 13. Chassaino, J. and Julien, P., Fluorures ternaires de gallium et de cadmium, de gallium et de manganese, C. R. Seances Acad. Sci., Ser. C, 1972, vol. 274, pp. 871-873.
- Ikrami, M.B., Sidorov, V.S., and Ruchkin, E.D., CdF₂-CoF₂ and CdF₂-NiF₂ Systems, *Zh. Neorg. Khim.*, 1988, vol. 33, no. 4, pp. 1074–1075.
- 15. Fedorov, P.P., Sattarova, M.A., Ol'khovaya, L.A., et al., Concerning the Polymorphism of Manganese Difluoride, Vysokochist. Veshchestva, 1991, no. 3, pp. 191–195.
- Buchinskaya, I.I., Fedorov, P.P., and Sobolev, B.P., PbF₂-Based Single Crystals and Phase Diagrams of PbF₂-MF₂ Systems (M = Mg, Ca, Sr, Ba, Cd), *Proc. SPIE-Int. Soc. Opt. Eng.*, 1996, vol. 3178, pp. 59-63.
- 17. Machulin, I.N., Nikolaev, S.V., Skorokhvatov, M.D., et al., New InF₃-Based Scintillating Materials for Neu-

trino Detection, Preprint of Kurchatov Inst. of Atomic Energy, Moscow, 1996, no. IAE-6016/2.

- Lagassie, P., Grannes, J., Omari, M.El., and Reau, J.M., Propriétés de conduction ionique des solutions solides Cd_{1-x}In_xF_{2+x} et Cd_{1-x}Bi_xF_{2+x}, *Rev. Chim. Miner.*, 1987, vol. 24, no. 3, pp. 328–337.
- 19. Termicheskie konstanty veshchestv: Spravochnik (Thermal Constants of Substances: A Handbook), Glushko, V.P., Ed., Moscow: VINITI, 1973, issue VI.
- Shannon, R.D., Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides, Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr., 1976, vol. 32, no. 5, pp. 751-767.
- Massa, W. and Babel, D., Crystal Structure and Bonding in Transition-Metal Fluoro Compounds, *Chem. Rev.* (Washington, D. C.), 1988, vol. 88, pp. 275–296.
- 22. Urusov, V.S., *Teoriya izomorfnoi smesimosti* (Theory of Isomorphous Miscibility), Moscow: Nauka, 1977.
- 23. Kravchuk, I.F., Experimental and Theoretical Studies of the Distribution of Isomorphous Impurities in Solidification of Binary Melts, *Cand. Sci. (Chem.) Dissertation*, Moscow, 1979.
- Urusov, V.S. and Dudnikova, V.V., Energetics of Heterovalent Microisomorphism with Subtraction (Vacancy Formation) in Ionic Crystals, *Geokhimiya*, 1987, no. 9, pp. 1219–1230.
- Urusov, V.S., Grigorash, Yu.P., Kazakevich, M.Z., and Karelin, V.V., Isovalent Isomorphism in Fluorite Structure Crystals, *Geokhimiya*, 1980, no. 11, pp. 1700–1709.
- Fedorov, P.P. and Sobolev, B.P., Some Features of Heterovalent Isomorphism with a Variable Number of Ions in the Unit Cell, VI Vsesoyuznyi simpozium po izomorfizmu (VI All-Union Symp. on Isomorphism), Zvenigorod, 1988, p. 202.
- 27. Fedorov, P.P., Sobolev, B.P., and Fedorov, P.I., Effect of Ionic Radii on the Formation of Heterovalent Solid Solutions with a Variable Number of Ions in the Unit Cell, *Kristallografiya*, 1981, vol. 26, no. 3, pp. 512–520.