FORMATION (DECOMPOSITION) ENTHALPY CALCULATIONS FOR CRYSTAL LATTICES OF ALKALINE-EARTH FLUORIDES

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A series of calculations of structural and thermochemical properties has been carried out for the alkaline-earth fluorides. The calculations have been carried out using the modified model of effective ionic radii and the model of enthalpy calculation for the crystal lattice. The results of the calculations are in accordance with the known experimental data within confidence intervals.

Keywords: alkaline-earth fluorides, enthalpy of formation, cation, electron, ionization potential, interstructural distance.

Introduction

Halogen compounds with other elements are widely used in technology, though fluorides are very different from other halides in their physicochemical properties.

Calcium fluoride (in a lesser degree, strontium fluoride and barium fluoride) is a major source of fluorine and its compounds. In chemical industry, more than half of all fluorite is spent for manufacture of hydrofluoric acid (HF), from which fluorinated organic and inorganic compounds, as well as artificial cryolite for aluminium industry, are obtained. The second biggest consumer of alkaline-earth fluorides is ferrous metallurgy, where they are used as fluxes in smelters. Calcium, strontium, and barium fluorides are components of special glasses, enamels, ceramics, optical and laser materials. Their monocrystals are usable in manufacture of windows, prisms, lenses and other optical details, which function in the radiation range from infrared to ultraviolet. Barium fluoride is used as a sorbent in UF_6 purification. Strontium fluoride is used as a component of solid-state fluoride ion batteries (FIBs) with high energy capacity and energy density [1].

According to the 2002 data, the world extraction of fluorspar equaled 4.5 million tons per year. And about a half of fluorite was produced in China. Mexico, South Africa, Mongolia were next with considerable lag. In Russia, consumption of fluorine raw material is about 270–300 thousand tons per year. However, at present the situation with supplies of industrial fluorite may be described as critical. The Russian enterprises, exploiting marginal deposits with low-quality product concentrate, are in the critical condition. In spite of the considerable reserves and resources of fluorite, there are not profitable deposits of high-quality fluorine raw material in reserves. Whereas the possibility of substitution of mineral fluorspar with suitable analogs is extremely low [2], therefore, the calculations of thermodynamic and structural properties of alkaline-earth metal fluorides become an investigation problem of urgent interest.

In the monograph [3], the basic concepts of the model of effective ionic radii and the model of enthalpy calculation for the crystal lattice are considered. The model of calculation of enthalpy of the crystal lattice allows carrying out calculations and obtaining values of the properties, which can not be obtained (with necessary accordance with other properties) at the present time: standard enthalpies of formation of multi-charged particles, ionization potentials, electron affinities, etc. In the present paper, on the example of alkaline-earth fluorides, the possibilities for complex uses of modified equations of the models in order to obtain concordance of the structural and thermochemical characteristics are demonstrated.

Initial data: alkaline-earth metal fluorides crystallize in the cubic crystal system (space group CaF_2, $F3m3-4$), the structure constant $\alpha = 0.4330127$; the Debye radius $r_D = r_{D\ CaF_2} \cdot f(z) \cdot f(c) = 15.18081 \times$ $\times\left(1+\sqrt{2\cdot 2\cdot 1-1}\right)\cdot 2\left(\sqrt{2}-1\right)=34.89582$; the minimum radius of fluoride ion $r^{\circ}\left(\mathrm{F}^{-}\right)=1.28960$; the enthalpy of gaseous fluoride ion formation $\Delta_f H^{\circ}\left(\mathrm{F}^{-},\mathrm{g}\right)=-255.148\pm0.270$ [3].

The enthalpy of formation (decomposition) of the crystal lattice of alkaline-earth fluorides is defined as

$$\Delta H_{\text{cr}}(\text{MeF}_2) = \Delta_f H^\circ(\text{Me}^{2+},\text{g}) + 2\cdot\Delta_f H^\circ(\text{F}^-,\text{g}) - \Delta_f H^\circ(\text{MeF}_2,\text{s}), \quad (1)$$

where $\Delta_f H^\circ(\text{Me}^{2+},\text{g})$ is the enthalpy of formation for a gaseous alkaline-earth metal cation; $\Delta_f H^\circ(\text{F}^-,\text{g})$ is the enthalpy of formation for a gaseous fluoride ion; $\Delta_f H^\circ(\text{MeF}_2,\text{s})$ is the enthalpy of formation for a crystalline alkaline-earth metal fluoride. After the substitution of the value $\Delta_f H^\circ(\text{F}^-,\text{g}) = -255.148\pm0.270$ [3] into equation (1), for MeF_2 we obtain

$$\Delta H_{\text{cr}}(\text{MeF}_2,\text{s}) = \Delta_f H^\circ(\text{Me}^{2+},\text{s}) - 510{,}296 + \Delta_f H^\circ(\text{MeF}_2,\text{s}). \quad (2)$$

Whereas the enthalpy of the crystal lattice ($\Delta H_{\text{cr}}(\text{MeF}_2)$) can be determined by using the basic calculation model of thermochemical properties [3].

The basic equation of the model

$$\Delta H_{\text{cr}} = \Delta H_0 + \Delta H_{\text{in}} \ . \quad (3)$$

The enthalpy of zero level, which is the starting point

$\Delta H_0 = 83.581728\ f_1(z)\cdot f_1(c)$,

where

$f_1(z) = (z_{\text{K}}^2\cdot n_{\text{K}})(z_{\text{A}}^2\cdot n_{\text{A}}) = (2^2\cdot 1)\cdot(1^2\cdot 2) = 8$;

$$f_1(c) = f_{\text{bcc}}\cdot f_{\text{fcc}} = \left(\frac{2}{\sqrt{3}}\right)^2\cdot\frac{\sqrt{2}}{2} = 0.942809\ .$$

Here z_{K} and z_{A} are the ion charges; n_{K} and n_{A} are the numbers of ions in a compound; f_{bcc} and f_{fcc} are the structure constants of initial and final (quasi-cubic) structures.

After the substitution of $f_1(z)$ and $f_1(c)$, we obtain $\Delta H_0 = 630.413$.

The enthalpy of the electromagnetic interaction

$\Delta H_{\text{in}} = 138.935405\cdot A_{\text{M}}\cdot\text{cn}\cdot f_2(z)\cdot f_2(c)\cdot r_{\text{d}}^{-1}$,

where $f_2(z) = (z_{\text{K}}\cdot n_{\text{K}})(z_{\text{A}}\cdot n_{\text{A}}) = (2\cdot 1)\cdot(1\cdot 2) = 4$;

$$f_2(c) = f_{\text{fcc}}\cdot f_{\text{tetr}} = \left(\frac{\sqrt{2}}{2}+1\right)\frac{3\sqrt{3}}{8} = 1.108798\ .$$

Here the coefficient 138.935405 is the combination of the fundamental constants; A_{M} is the Madelung constant; nc is the coordination number; f_{fcc} and f_{tetr} are the structural characteristics of the initial and quasi-cubic structures; r_d is the interparticle (interstructural) distance.

Then

$$\Delta H_{\text{in}} = 138.935405\cdot 1.259695\cdot 6\cdot 4\cdot 1.108798\cdot r_{\text{d}}^{-1} = 4657.3853\ r_{\text{d}}^{-1}\ . \quad (4)$$

Finally, for alkaline-earth metal fluorides equation (3) becomes

$$\Delta H_{\text{cr}} = 630.413 + 4657.3853\ r_{\text{d}}^{-1}\ . \quad (5)$$

The joint solution of equations (2) and (5) allows refining the known thermochemical data for alkaline-earth fluorides, as well as carrying out the predicting calculations for the unknown values.

In order to use equations (2) and (5), it is necessary to know the following parameters: the enthalpy of formation for a gaseous cation $\Delta_f H^\circ(\text{Me}^{2+},\text{g})$, the enthalpy of formation for a crystalline fluoride $\Delta_f H^\circ(\text{MeF}_2,\text{s})$, and the interstructural distance (r_d). Techniques of calculations of these structural and thermal characteristics are considered further.

1. Enthalpy of formation of alkaline-earth cations in the gaseous phase

By definition, the equation for standard enthalpy of formation of the metal cations is as follows:

$$\Delta_f H^\circ\left(\mathrm{Me}^{z+},\mathrm{g},298\right)=\Delta_f \mathrm{H}^\circ\left(\mathrm{Me}^0,\mathrm{g},298\right)+\sum^{z} I+6.1965\cdot z\,. \qquad (6)$$

I is the ionization potential, kJ[1]; 6.1965 is the molar enthalpy of electron gas formation [2].

The results of the calculations from the equation (6) and the input (reference data) are set out in Table 1. The obtained values of $\Delta_f H^\circ\left(\mathrm{Me}^{2+},\mathrm{g}\right)$ are used in the calculation of ΔH_1 from equation (2).

Table 1

Standard enthalpy of formation of double-charged alkaline-earth cations in the gaseous phase

Me $r(\mathrm{Me}^{2+})$, [2]	$\Delta_f H^\circ\left(\mathrm{Me}^0,\mathrm{g}\right)$, [4, 5]	I_1, eV, [4] I_1, eV, [4]	$\sum^{2} I$, kJ	$\Delta_f H^\circ\left(\mathrm{Me}^{2+},\mathrm{g}\right)$, eq. (6)
1	2	3	4	5
Ca 1.01202	147.790±1.674	$6.11308_{(10)}$ $11.8714_{(3)}$	1735.225±0.013	1895.408±1.687
Sr 1.15779	165.686±2.092	$5.69410_{(8)}$ $11.0302_{(1)}$	1613.637±0.087	1791.716±2.197
Ba 1.36361	180.749±4.184	$5.21140_{(8)}$ $10.0040_{(5)}$	1468.051±0.013	1661.193±4.197
Ra 1.38269	157.737±2.092	$5.2790_{(6)}$ $10.1472_{(2)}$	1488.390±0.077	1658.520±2.169

2. Enthalpy of formation of alkaline-earth fluorides

The reference data of $\Delta_f \mathrm{H}^\circ\left(\mathrm{MeF}_2,\mathrm{s}\right)$ (Table 2, column 3) allow the use of the model of standard enthalpy of formation of compounds [3]. According to the model for the similar substances, which are crystallized in one and the same crystal system, the specific enthalpy of formation (h) is directly proportional to the relative charge of the metal atom nucleus (z_e).

$$h=\frac{-\Delta_f H}{\Sigma z}\,. \qquad (7)$$

$$z_\mathrm{e}=\frac{z_\mathrm{Me}}{\Sigma z}\,. \qquad (8)$$

This dependency is described by the following linear equation:

$$h=h_0+k\,z_\mathrm{e}\,. \qquad (9)$$

The results of the calculations are set out (Table 2, columns 6, 7). Reference data (column 3) and the results of $\Delta_f \mathrm{H}^\circ\left(\mathrm{MeF}_2,\mathrm{s}\right)$ calculation are consistent with each other, which validates the model.

Table 2

Standard enthalpy of formation of crystalline alkaline-earth fluorides

MeF_2	Σz	$-\Delta_f \mathrm{H}^\circ\left(\mathrm{MeF}_2,s\right)$, [1, 6]	h, eq. (7)	z_e, eq. (8)	h, eq. (9)	$-\Delta_f \mathrm{H}^\circ\left(\mathrm{MeF}_2,\mathrm{s}\right)$, eq. (6)
1	2	3	4	5	6	7
CaF_2	38	1214.6	31.963158	0.526316	31.963158	1214.600
SrF_2	56	1209.6	21.60000	0.67857	21.600045	1209.603
BaF_2	74	1204.6	16.278378	0.756757	16.278378	1204.600
RaF_2	106	1195.8	11.280288	0.830189	11.280288	1195.711

[1]The first two ionization energy values I for many metals are known with high accuracy, but the accuracy of $\Delta_f \mathrm{H}^\circ\left(\mathrm{Me}^0,g,298\right)$ is much lower.

3. Enthalpy of formation (decomposition) of alkaline-earth fluoride crystal lattice

To derive ΔH_1 from equation (5) it is necessary to know the values of interstructural distances r_p, so the alkaline-earth metal fluorides structural characteristics calculation technique is explained below on the example of strontium fluoride SrF_2. The lattice constant is a =5.7800.

1. The interstructural distance is calculated as follows:

$$r_p = \alpha \cdot a = 0.4330127 \cdot 5.7800 = 2.50281. \quad (10)$$

2. The ion radius $r(F^-)$ is evaluated by the following:

$$r(F^-) = r_d - r(Sr^{2+}) = 2.50281 - 1.15779 = 1.34502. \quad (11)$$

3. The minimum ion radius $r^\circ(F^-)$ is calculated according to the formula:

$$r^\circ(F^-) = \left[-\frac{1}{2} \frac{r(Sr^{2+}) r_D}{(r_d - r(Sr^{2+}))} \right] + \left[\left(\frac{r(Sr^{2+}) r_D}{2(r_d - r(Sr^{2+}))} \right)^2 + r(Sr^{2+}) r_D \right]^{1/2} = 1.28959. \quad (12)$$

The results of calculation for strontium fluoride SrF_2 and other alkaline-earth fluorides structural characteristics are shown in Table 3.

Table 3

Structural characteristics of crystalline alkaline-earth fluorides

Me $r(Me^{2+})$, [2]	a, [1, 6]	r_d, eq. (10)	$r(F^-)$, eq. (11)	$r^\circ(F^-)$, eq. (12)
1	2	3	4	5
Ca 1.01202	5.4626	2.36538	1.35336	1.28961
Sr 1.15779	5.7800	2.50281	1.34502	1.28959
Ba 1.36361	6.2352	2.69983	1.33622	1.28960
Ra 1.38269	6.2777	2.71832	1.33563	1.28960

The values of $r^\circ(F^-)$ (Table 3, column 6) show the self-consistency and the equality with the value of the minimum ion radius of F^- in the alkaline halides, which have been calculated earlier [3]. It strengthens the model validation and allows using values r_p to calculate the lattice enthalpy of ΔH_1.

The results of decomposition enthalpy calculation of crystalline alkaline-earth fluorides are suggested in Table 4.

Table 4

Decomposition enthalpy of crystalline alkaline-earth fluorides.

MeF_2	r_d^{-1}, (Table 3)	$\Delta_f H^\circ(Me^{2+}, g)$, (Table 1)	$-\Delta_f H^\circ(MeF_2, s)$, (Table 2)	ΔH_1, eq. (2)	ΔH_1, eq. (4)	ΔH_1, eq. (5)
1	2	3	4	5	6	7
CaF_2	0.422770	1895.408±1.687	1214.6	2599.712±2.227	1969.003	2599.416
SrF_2	0.399551	1791.716±2.197	1209.6	2491.023±2.719	1860.863	2491.276
BaF_2	0.370394	1661.193±4.197	1204.6	2355.497±4.737	1725.068	2355.481
RaF_2	0.367874	1658.520±2.169	1195.8	2343.935±2.246	1713.331	2343.744

The data of column 5 and 7 are consistent, which validates the used model.

Conclusion

The decomposition enthalpies of alkaline-earth fluorides are calculated by classical thermodynamic equation and by the model of lattice enthalpy equation suggested by A.G. Ryabukhin. The calculation results are fairly well consistent with each other, which proves the correctness of the used model as applied to similar systems. The technique of calculation of intermediate structural and thermal characteristics (enthalpy of formation of alkaline-earth cations in the gaseous phase, enthalpy of formation of crystalline alkaline-earth metal fluorides, interstructural distance) is shown.

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РАСЧЕТЫ ЭНТАЛЬПИИ ОБРАЗОВАНИЯ (РАЗРУШЕНИЯ) КРИСТАЛЛИЧЕСКОЙ РЕШЕТКИ ФТОРИДОВ ЩЕЛОЧНОЗЕМЕЛЬНЫХ МЕТАЛЛОВ

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Для фторидов щелочноземельных металлов проведена серия расчетов структурных и термохимических характеристик. Расчеты проведены с использованием модифицированной модели эффективных ионных радиусов и модели расчета энтальпии кристаллической решетки. Результаты вычислений согласуются с имеющимися экспериментальными данными в пределах доверительных интервалов.

Keywords: фториды, щелочноземельные металлы, энтальпия образования, катион, электрон, потенциал ионизации, межструктурное расстояние.

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