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Energetics of formation of KF–GdF$_3$ binary-intermediate compounds

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Abstract

Enthalpies of formation were measured for KGdF$_4$, K$_2$GdF$_5$ and KGd$_2$F$_7$ using the transposed temperature drop calorimetry method. These compounds were synthesized by conventional solid state reaction methods using mixtures of KF and GdF$_3$. The measured enthalpies of formation from fluorides for KGdF$_4$, K$_2$GdF$_5$ and KGd$_2$F$_7$ were -22.3, -16.1 and -18.3 kJ mol^{-1}, respectively. From these measurements, enthalpies of formation from the elements were computed to be -2290.0, -2852.4 and -3985.2 kJ mol^{-1} for the respective compounds. These enthalpies were compared with estimated values calculated by two methods previously reported to be effective for multicomponent oxides. Estimated values compare favorably with measured data, with deviations ranging from 0.5 to 2.9%. The errors of 0.5–2.9% correspond to a 16–85 kJ mol^{-1} uncertainty range for $\Delta_f H^0$ of ternary fluorides from binary fluorides. One of these methods, based on the summation of $\Delta_f H^0$ values for the constituent binary fluorides, is recommended for the K–Gd–F compounds.

Keywords: Calorimetry; Enthalpy of formation; Estimation; Optical materials; Ternary fluorides

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1. Introduction

Multicomponent fluorides have tremendous potential for use in passive and active optical materials. As passive materials, the glassy heavy metal fluorides exhibit excellent infrared transparency with a projected loss minimum that exceeds that of intrinsic silica by two orders of magnitude [1]. As active materials, the broad transparency window and longer wavelength phonon spectra facilitate rare earth fluorescence energies that have never been observed in oxides. Both crystals and glassy materials have been studied extensively for such purposes [2,3].

In order to develop useful processes for making fluoride materials as well as to identify compounds that have suitable chemical durability, thermodynamic data are essential. In this paper, attention will be focused on the thermochemical properties of the family of compounds in the KF–GdF_3 system: $KGdF_4$, K_2GdF_5 and KGd_2F_7.

While phase equilibria of the KF–GdF_3 system have been reported for both solid–gas [4–6] and hydrothermal solid–liquid [3] systems, no thermochemical data have been reported for these compounds. Furthermore, estimation methods for such fluoride systems have not been reported either. Thus, the objectives of this paper are to provide reliable thermochemical data and to identify an estimation procedure by which such data can be predicted for the KF–GdF_3 system as well as for other multicomponent fluorides.

2. Experimental

The compounds $KGdF_4$, K_2GdF_5, and KGd_2F_7 were each synthesized by a conventional solid state reaction method. KF (Alfa/Johnson Matthey, Ward Hill, MA, 99.99%, anhydrous) and GdF_3 (Alfa/Johnson Matthey, 99.99%, anhydrous) were mixed in three batches corresponding to the ratios of 1:1, 2:1 and 1:2 using a mortar and pestle. The various fluorides were reacted in a platinum boat at 923 K in a muffle furnace for 36–48 h, which was operated in a nitrogen filled glovebox. X-ray diffraction for each sample indicated the formation of phase-pure $KGdF_4$, K_2GdF_5, and KGd_2F_7 with patterns similar to those of materials synthesized hydrothermally by Bridenbaugh et al. [3].

The goal of the calorimetric experiments was to determine enthalpies of high temperature reactions, which convert the ternary fluoride and a corresponding stoichiometric mixture of binary fluorides to the same thermodynamic final state. Considering the KF–GdF_3 phase diagram [4,5] and the capabilities of our high temperature calorimeters, the liquid state at 1073 K was chosen as this final state. At this temperature, the fluoride compositions chosen melted quickly and completely. Using samples in welded gold capsules (see below) eliminates any problems of volatile loss and reaction with the atmosphere. These direct melting experiments produced heats of fusion, from which heats of formation from the fluorides were directly calculated. Enthalpies of formation from the elements were then calculated using reference values for the binary fluorides taken from the compilation of Barin [7].

Heat-content measurements were accomplished using a high-temperature hybrid calorimeter [8]. This calorimeter combines the advantages of the Calvet twin and Setaram HT-1500 calorimeters. The samples, each ~ 80 mg, were sealed in gold capsules in a dry box at room temperature and dropped into the calorimeter at 1073 K. Data were acquired by a PC equipped with an IEEE-488 interface board (GPIB). Calibration was established by dropping known masses of platinum. Calibration experiments produced standard deviations of ~ ± 1%. Each sample was dropped three times. Enthalpy measurements on crystalline compounds, i.e., $KGdF_4$ and KGd_2F_7, that have higher melting points than the temperature of the experiment (1073 K) were performed by a method similar to that developed to measure the enthalpy of formation of $NaMgF_3$ [8]. This technique converts both reactants and products to the same final molten state by dropping a mixture of the reactant or product plus a known excess of one of the components to produce a near-eutectic bulk composition. For example, KF was added to $KGdF_4$ to bring the overall molar composition to 66.67% KF, which is close to one of the two eutectic points in the KF–GdF_3 system (1001 K at 63% KF). This composition ensured rapid mixing and formation of a homogeneous liquid in the calorimeter at 1073 K. Enthalpies measured for the fusion reactions and the heats of formation from the binary fluorides are listed in Table 1.

The drop of the mechanical mixture of KF and GdF_3 is represented by the following reaction

$$2\mathrm{KF(cr, 298.15)} + \mathrm{GdF_3(cr, 298.15)} \xrightarrow{\Delta_r H_1} 2\mathrm{KF{\cdot}GdF_3(l, 1073)} \quad (1)$$

The drop of the second type of sample, a mixture of $KGdF_4$ and KF, is represented by

$$\mathrm{KGdF_4(cr, 298.15)} + \mathrm{KF(cr, 298.15)} \xrightarrow{\Delta_r H_2} 2\mathrm{KF{\cdot}GdF_3(l, 1073)} \quad (2)$$

Table 1
Results of calorimetric measurements for $KGdF_4$, K_2GdF_5, and KGd_2F_7

Fusion reactions	$\Delta_r H/\mathrm{kJ\ mol^{-1}}$
$2\mathrm{KF(cr, 298.15)} + \mathrm{GdF_3(cr, 298.15)} \rightarrow 2\mathrm{KF{\cdot}GdF_3(l, 1073)}$	209.3 ± 2.7^{a}
$\mathrm{KGdF_4(cr, 298.15)} + \mathrm{KF(cr, 298.15)} \rightarrow 2\mathrm{KF{\cdot}GdF_3(l, 1073)}$	231.6 ± 2.7^{a}
$\mathrm{K_2GdF_5(cr, 298.15)} \rightarrow 2\mathrm{KF{\cdot}GdF_3(l, 1073)}$	225.4 ± 1.7^{a}
$\mathrm{KGd_2F_7(cr, 298.15)} + 3\mathrm{KF(cr, 298.15)} \rightarrow 2(2\mathrm{KF{\cdot}GdF_3})\mathrm{(l, 1073)}$	436.9 ± 4.2^{a}
Formation reaction from fluorides	$\Delta_r H^0/\mathrm{kJ\ mol^{-1}}$
$\mathrm{KF(cr, 298.15)} + \mathrm{GdF_3(cr, 298.15)} \rightarrow \mathrm{KGdF_4(cr, 298.15)}$	-22.3 ± 3.5^{b}
$2\mathrm{KF(cr, 298.15)} + \mathrm{GdF_3(cr, 298.15)} \rightarrow \mathrm{K_2GdF_5(cr, 298.15)}$	-16.1 ± 2.8^{b}
$\mathrm{KF(cr, 298.15)} + 2\mathrm{GdF_3(cr, 298.15)} \rightarrow \mathrm{KGd_2F_7(cr, 298.15)}$	-18.3 ± 5.3^{b}

[a] Uncertainties on measurements represent twice the standard deviation of the mean [9].

[b] Uncertainty calculated as the square root of the sum of the squares of the values for the individual reactions.

The final state is the same in both reactions. The difference between these two reactions gives

$$\mathrm{KF(cr, 298.15)} + \mathrm{GdF_3(cr, 298.15)} \xrightarrow{\Delta_r H_3} \mathrm{KGdF_4(cr, 298.15)} \quad (3)$$

so $\Delta_r H_3 = \Delta_r H_1 - \Delta_r H_2$, where $\Delta_r H_3$ is the enthalpy of formation of $KGdF_4$ from the binary end-member fluorides at 298.15 K. The same approach was applied to the enthalpy measurement of KGd_2F_7.

For K_2GdF_5, which has a lower melting temperature than the calorimetric temperature, a simple direct-drop method was used. The relevant thermodynamic cycle is

$$\mathrm{K_2GdF_5(cr, 298.15)} \xrightarrow{\Delta_r H_4} \mathrm{2KF{\cdot}GdF_3(l, 1073)} \quad (4)$$

$$\mathrm{2KF(cr, 298.15)} + \mathrm{GdF_3(cr, 298.15)} \xrightarrow{\Delta_r H_5} \mathrm{2KF{\cdot}GdF_3(l, 1073)} \quad (5)$$

Again, the final state is the same in both reactions. The difference between these two reactions gives

$$\mathrm{2KF(cr, 298.15)} + \mathrm{GdF_3(cr, 298.15)} \xrightarrow{\Delta_r H_6} \mathrm{K_2GdF_5(cr, 298.15)} \quad (6)$$

Thus, $\Delta_r H_6 = \Delta_r H_5 - \Delta_r H_4$, where $\Delta_r H_6$ is the enthalpy of formation of K_2GdF_5 from the fluorides at 298 K.

3. Estimation methods

Although we have experimentally obtained the enthalpies of formation of $KGdF_4$, K_2GdF_5 and KGd_2F_7, it is worthwhile to examine independent methods for their prediction in order to check the conformity of the obtained values with generally observed trends. Various methods for the estimation of the Gibbs energy of formation from the elements ($\Delta_f G^0$) for solid compounds have been reviewed by Nordstrom and Munoz [10] and, later, by Sverjensky [11]. Most methods introduce uncertainties of about $\pm(20\text{–}40)$ kJ mol^{-1} [12] unless they are restricted to isostructural families of crystalline solids. In general, the availability of thermochemical data for multicomponent fluorides is very limited thus making it impossible to create isostructural families. Therefore, in our work, Gibbs energies of formation of multicomponent fluorides are estimated by using a method that was previously developed to predict $\Delta_f G^0$ values for a variety of oxides, i.e., hydroxides, silicates, phosphates, sulfates, nitrates and carbonates [13–16]. Then, enthalpies of formation for those compounds are calculated using estimated entropies and are compared to measured $\Delta_f H^0$ values. For comparison, we made an attempt to calculate the enthalpies of formation of ternary fluorides as a sum of those for binary fluorides. This is justified by the fact that the enthalpies of formation of $KGdF_4$, K_2GdF_5 and KGd_2F_7 from their constituent fluorides are relatively small (see Table 1).

The first method, previously used for multicomponent oxides, is based on the knowledge of $\Delta_f G^0$ of the constituent oxides and metal cations. The original equation of Tardy and Vieillard [14] for multicomponent oxides is

$$\Delta\text{compound} = \alpha\frac{n_1 n_2}{n_1 + n_2}(\Delta O^{2-}(\text{Me}) - \Delta O^{2-}(\text{Me}_{\text{ref}})) \quad (7)$$

where Δcompound is equal to the difference between the Gibbs energy of formation of the solid compound and those for the corresponding oxides

$$\Delta\text{compound} = \Delta_f G^0(\text{compound}) - \Sigma\, \Delta_f G^0(\text{oxides}) \quad (7a)$$

and n_1 and n_2 are the numbers of oxygen atoms required to balance the cation of interest and the reference cation in the formula of the multicomponent oxide, respectively.

Relationship (7) is linear with respect to the product $(n_1 n_2/(n_1 + n_2))(\Delta O^{2-}(\text{Me}) - \Delta O^{2-}(\text{Me}_{\text{ref}}))$ and α is a proportionality constant that is characteristic of a family of compounds. A multicomponent oxide consists of two metals: the metal cation of interest (Me) and a reference metal cation (Me_{ref}) that is common in the family of solids. $\Delta O^{2-}(\text{Me})$ is a parameter for the cation of interest, which is expressed as a difference between $\Delta_f G^0$ of its corresponding crystalline oxide, $\Delta_f G^0(\text{MeO}_{z/2}, \text{cr})$, and that for the aqueous cation, $\Delta_f G^0(\text{Me}^{z+}, \text{aq})$

$$\Delta O^{2-}(\text{Me}) = (2/z)(\Delta_f G^0(\text{MeO}_{z/2}, \text{cr}) - \Delta_f G^0(\text{Me}^{z+}, \text{aq})) \quad (7b)$$

where z is the charge number on the cation of interest. The same expression is valid for the parameter $\Delta O^{2-}(\text{Me}_{\text{ref}})$ for the reference cation.

In this work, we adapt this method to multicomponent fluorides. When applied to fluorides of a general formula $x(\text{MeF}_a)\cdot y(\text{Me}_{\text{ref}}\text{F}_b)$, Eq. (7) takes the form

$$\Delta_f G^0(x(\text{MeF}_a)\cdot y(\text{Me}_{\text{ref}}\text{F}_b), \text{cr}) - x\Delta_f G^0(\text{MeF}_a, \text{cr}) - y\Delta_f G^0(\text{Me}_{\text{ref}}\text{F}_b, \text{cr})$$

$$= \alpha\frac{n_1 n_2}{n_1 + n_2}(\Delta F(\text{Me}) - \Delta F(\text{Me}_{\text{ref}})) \quad (8)$$

where $n_1 = x\,a$, $n_2 = y\,b$ and

$$\Delta F(\text{Me}) = (1/a)[\Delta_f G^0(\text{MeF}_a, \text{cr}) - \Delta_f G^0(\text{Me}^{a+}, \text{aq})] \quad (8a)$$

The same expression is valid for Me_{ref}

$$\Delta F(\text{Me}_{\text{ref}}) = (1/b)[\Delta_f G^0(\text{Me}_{\text{ref}}\text{F}_b, \text{cr}) - \Delta_f G^0(\text{Me}^{b+}, \text{aq})] \quad (8b)$$

All of the investigated compounds contain K^+ as a common cation. Therefore, to use this method for $KGdF_4$, K_2GdF_5 and KGd_2F_7, thermochemical data for multicomponent fluorides containing K^+ as a reference cation (Me_{ref}) are required. These data should contain $\Delta_f G^0$ of the cation K^+ and all considered metal cations (Me^{a+}), those of KF ($\text{Me}_{\text{ref}}\text{F}_b$) and all constituent fluorides (MeF_a), and those of multicomponent fluorides $x(\mathrm{MeF}_a)\cdot y(\mathrm{KF})$. For our particular case, Eq. (8) becomes

$$\Delta_f G^0(x(\mathrm{MeF}_a)\cdot y(\mathrm{KF}), \mathrm{cr}) - x\Delta_f G^0(\mathrm{MeF}_a, \mathrm{cr}) - y\Delta_f G^0(\mathrm{KF}, \mathrm{cr})$$

$$= \alpha\frac{n_1 n_2}{n_1 + n_2}(\Delta F(\mathrm{Me}^{a+}) - \Delta F(\mathrm{K}^+)) \tag{9}$$

where

$$\Delta F(\mathrm{Me}^{a+}) = (1/a)(\Delta_f G^0(\mathrm{MeF}_a, \mathrm{cr}) - \Delta_f G^0(\mathrm{Me}^{a+}, \mathrm{aq})) \tag{9a}$$

and

$$\Delta F(\mathrm{K}^+) = (\Delta_f G^0(\mathrm{KF}, \mathrm{cr}) - \Delta_f G^0(\mathrm{K}^+, \mathrm{aq})) \tag{9b}$$

To establish the linear relation represented by Eq. (9), we use thermochemical data for four ternary fluorides: K_3AlF_6, $KCdF_3$, $KZnF_3$ and $KMgF_3$. The data for K_3AlF_3 are known from thermochemical tables [7] and the enthalpies of formation from fluorides for $KCdF_3$, $KZnF_3$ and $KMgF_3$ at high temperature are available from calorimetric measurements [17–19]. To calculate $\Delta_f H^0$ for these fluorides at the reference temperature, 298.15 K, we need to know the $\Delta_f H^0$ values of the constituent fluorides, i.e., CdF_2, ZnF_2 and MgF_2 at 298.15 K and the heat capacities of $KCdF_3$, $KZnF_3$ and $KMgF_3$ as functions of temperature. All necessary data for binary fluorides are available from thermochemical tables [7] while the C_p^0 values are estimated from the Kubaschewski–Ünal [20] group contribution method. According to Kubaschewski and Ünal [20], the heat capacities of $KCdF_3$, $KZnF_3$ and $KMgF_3$ are calculated from the Kelley equation

$$C_p^0 = a + bT + cT^{-2} \tag{10}$$

where the coefficients a, b and c are calculated as

$$a = (10^{-3}T_m(\Sigma C_{pi}^0 + 4.7n) - 1.25n\,10^5\,T_m^{-2} - 9.05\,n)/(10^{-3}\,T_m - 0.298) \tag{10a}$$

$$b = (25.6\,n + 4.2\,n\,10^5\,T_m^{-2} - \Sigma\,C_{pi}^0)/(10^{-3}\,T_m - 0.298) \tag{10b}$$

$$c = -4.2\,n \tag{10c}$$

T_m is the absolute melting temperature of the compound and n is the corresponding number of ionic entities in the formula. ΣC_{pi}^0 is calculated from cationic and anionic contributions to the molar heat capacity of the solid compound at 298.15 K. Having obtained $\Delta_f H^0$ for $KCdF_3$, $KZnF_3$ and $KMgF_3$, we can estimate their Gibbs energy of formation if the entropy is known. Entropies of complex solid compounds can be estimated by various methods [10, 21–24]. Since little information exists concerning the entropies (S^0) of multicomponent fluorides, some of these methods [22, 23] cannot be applied for our purposes. At the same time, the Latimer ionic contributions method [21] is not recommended for Mg-containing species [22] or for lanthanide compounds [25]. Therefore, in our work we calculated the entropy of multicomponent fluorides as a sum of those for the constituent fluorides. For comparison, we also applied the method developed by Fyfe [22] and modified by Helgeson [23] and, later, by Holland [24]. In this method, the difference between the entropy and molar volume for the compound of interest is equal to the sum of those for the constituent oxides or, in our case, fluorides. Both methods give very similar results with a maximum difference of 2 J K^{-1} mol^{-1}. Finally, we can calculate the unknown $\Delta_f G^0$ for the fluorides of interest, i.e., $KGdF_4$, K_2GdF_5 and KGd_2F_7, using the obtained linear relationship (see (Eq. (9)) because the thermochemical data for GdF_3 and Gd^{3+} are available in the literature [7, 26].

4. Results and discussion

Enthalpies of fusion have been calorimetrically measured for all reactions that are necessary to compute the enthalpy of formation from flourides for $KGdF_4$, K_2GdF_5 and KGd_2F_7. All fusion reactions and the corresponding enthalpies are collected in Table 1. The enthalpies of formation from the fluorides at 298.15 K are -22.3 ± 3.5 kJ mol^{-1} for $KGdF_4$, -16.1 ± 2.8 kJ mol^{-1} for K_2GdF_5 and -18.3 ± 5.3 kJ mol^{-1} for KGd_2F_7. The enthalpies of formation from the elements have been calculated using the available enthalpies of formation for solid KF and GdF_3 (see Table 2). The obtained enthalpies of formation for $KGdF_4$, K_2GdF_5 and KGd_2F_7 are equal to -2290.0, -2852.4 and -3958.2 kJ mol^{-1}, respectively. The uncertainties in these values arise from both the standard deviations of our calorimetric measurements and from the uncertainties in the enthalpies of formation of the binary fluorides from the elements which can be estimated at ± 0.4 kJ mol^{-1} for KF and ± 2.3 KJ mol^{-1} for GdF_3 according to Chase et al. [27] and Flotow and O'Hare [28], respectively. The total magnitude of the uncertainty can be estimated at $\pm 5 - \pm 8$ kJ mol^{-1}.

In the estimation procedure outlined above, the necessary thermochemical data, i.e., $\Delta_f G^0$. $\Delta_f H^0$ and S^0, for the solid compounds were taken from the compilation of Barin [7] and are shown in Table 2. The data compilation of Barin [7] has been chosen because it contains all solid species of our interest. The values of the thermochemical

Table 2
Thermochemical properties at 298.15 K for the species that are used in the calculations

Species	$\Delta_f G^0$/ kJ mol^{-1}	$\Delta_f H^0$/ kJ mol^{-1}	S^0/ J mol^{-1} K^{-1}	Ref.	Species	S^0/ J mol^{-1} K^{-1}	Ref.
KF(cr)	−538.934	−568.606	66.546	[7]	K(cr)	64.670	[7]
CdF_2(cr)	−649.444	−700.402	83.680	[7]	Cd(cr)	51.789	[7]
ZnF_2(cr)	−713.509	−764.417	73.680	[7]	Zn(cr)	41.631	[7]
MgF_2(cr)	−1071.106	−1124.241	57.255	[7]	Mg(cr)	32.677	[7]
AlF_3(cr)	−1431.096	−1510.400	66.480	[7]	Al(cr)	28.275	[7]
GdF_3(cr)	−1622.387	−1699.122	114.771	[7]	Gd(cr)	67.948	[7]
K_3AlF_6(cr)	−3163.443	−3326.280	284.512	[7]	F_2(g)	202.795	[7]
K^+(aq)	−282.462	−252.170	101.044	[26]	H_2(g)	130.680	[7]
Cd^{2+}(aq)	−77.655	−75.898	−72.802	[26]			
Zn^{2+}(aq)	−147.277	−153.385	−109.621	[26]			
Mg^{2+}(aq)	−453.985	−465.960	−138.072	[26]			
Al^{3+}(aq)	−483.700	−530.670	−325.100	[26]			
Gd^{3+}(aq)	−663.582	−687.013	−205.853	[26]			

properties from the above compilation [7] are in very good agreement with those from other sources [27, 29–31]. Thermochemical data for ionic species were taken from the compilation of Shock and Helgeson [26] because it contains all species of interest (see Table 2). In general, the data of Shock and Helgeson [26] for ionic species agree with those of Barin [7].

Estimated heat capacities and coefficients in Eqs. (10, 10a–c) are collected in Table 3. All thermochemical data for K_3AlF_6 were obtained from the compilation of Barin [7]. The standard enthalpies of formation from the elements calculated for $KCdF_3$, $KZnF_3$ and $KMgF_3$ on the basis of high-temperature enthalpies from constituent fluorides [17–19] are shown in Table 4. Also given are absolute entropies calculated using the sum of entropies of constituent fluorides and the resulting Gibbs energies of formation. Once all necessary data are collected or estimated, the parameters $\Delta F(K^+)$ in Eq. (9b) and $\Delta F(Me^{a+})$ for Cd, Zn, Mg and Al in Eq. (9a) can be calculated. The difference between the $\Delta_f H^0$ values of K_2AlF_6, $KCdF_3$, $KZnF_3$ or $KMgF_3$ and that of their constituent fluorides is linear as shown in Fig. 1. The α coefficient (Eq. (9)) is equal to 1.30 and the regression coefficient is 0.99.

For $KGdF_4$, K_2GdF_5 and KGd_2F_7, we can calculate values on the right-hand side of Eq. (9) using the data for KF, GdF_3, K^+ and Gd^{3+} from Table 2. Then, the unknown Gibbs energies of formation from the elements are calculated using the $\Delta_f G^0$ values of GdF_3 and KF. Finally, enthalpies of formation are calculated based on the estimated entropies. The obtained values are shown in Table 5. They are compared to the experimental enthalpies, and a relative deviation is also given. The deviation ranges from 1.3 to 2.9%. These differences are satisfactory in terms of being a small percentage

Table 3
Input parameters and coefficients of Eqs. (10) and (10a–c) for the compounds used in the heat capacity calculations

Compound	T_m/ K	Ref.	ΣC^0_{pi}/ J mol^{-1} K^{-1}	n	a/ J mol^{-1} K^{-1}	$b \times 10^3$/ J mol^{-1} K^{-2}	$c \times 10^{-5}$/ J mol^{-1}K
$KCdF_3$(cr)	1222	[17]	117.3	5	136.785	13.1021	−21
$KZnF_3$(cr)	1140	[18]	116.1	5	134.695	16.0521	−21
$KMgF_3$(cr)	1343	[19]	114.0	5	133.078	14.5113	−21

Table 4
Thermochemical data at 298.15 K calculated from high-temperature calorimetric data and estimation methods

Compound	$\Delta_f H^0_{exp}$/ kJ mol^{-1}	S^0_{est}/ J mol^{-1} K^{-1}	$\Delta_f G^0_{calc}$/ kJ mol^{-1}
$KCdF_3$(cr)	−1296.0	150.23	−1215.3
$KZnF_3$(cr)	−1358.3	140.23	−1277.7
$KMgF_3$(cr)	−1718.2	123.80	−1635.4

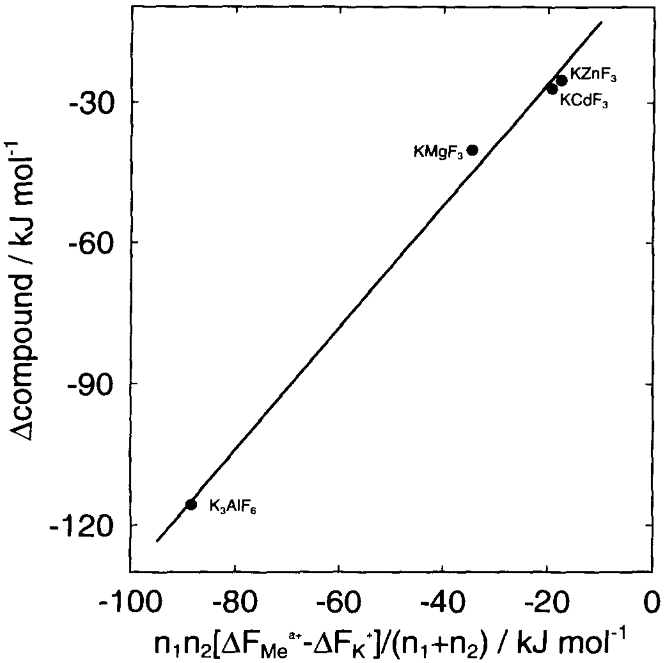

Fig. 1. Correlation of the Gibbs energies of formation for the ternary fluorides as defined by Eq. (9).

Table 5
Experimental and calculated thermochemical properties at 298.15 K of the potassium gadolinium fluorides

Species	$\Delta_f H^0_{exp}$ / kJ mol^{-1}	$\Delta_f G^0_{est}$/ kJ mol^{-1}	S^0_{est}/ J mol^{-1} K^{-1}	$\Delta_f H^0_{calc}$ [a]/ kJ mol^{-1}	AAD[b]/ %	$\Delta_f H^0_{calc}$ [c]/ kJ mol^{-1}	AAD[b]/ %
$KGdF_4$(cr)	−2290.0	−2222.9	181.32	−2329.3	1.7	−2267.7	0.97
K_2GdF_5(cr)	−2852.4	−2798.7	247.86	−2934.8	2.9	−2836.3	0.56
KGd_2F_7(cr)	−3985.2	−3854.1	296.09	−4037.2	1.3	−3966.9	0.46

[a] Calculated according to Eq. (9).
[b] ADD = $|1 - \Delta_f H^0(\mathrm{calc})/\Delta_f H^0(\mathrm{exp})| \times 100$.
[c] Calculated by summation of $\Delta_f H^0$ for constituent binary fluorides.

of the total $\Delta_f H^0$ and their absolute values are 40–85 kJ mol^{-1} (see Table 5). This is in reasonable agreement with uncertainties that are introduced by most general estimation methods of $\Delta_f G^0$. However, the predictions could be more accurate if more than four data points were used for developing the correlation (see Eq. (9)) and if no estimations of entropies and heat capacities were necessary.

Since the heats of formation of the ternary fluorides from binary fluorides in the KF–GdF_3 system are only about 20 kJ mol^{-1} (Table 1), we can make a simple assumption that the $\Delta_f H^0$ for $KGdF_4$, K_2GdF_5 and KGd_2F_7 can be calculated as a sum of those for constituent binary fluorides. The results are shown in Table 5 and better agreement with measured values is obtained than from the first method. In this case, the uncertainties vary from 0.5 to 1.0% which corresponds to 16–22 kJ mol^{-1} and is comparable with the measured enthalpies of formation from fluorides. We can conclude that the straight summation method gives better results for K–Gd–F compounds although, in general, both methods can be used for the prediction of thermochemical data of complex fluorides.

5. Conclusions

Enthalpies of formation from the elements of $KGdF_4$, K_2GdF_5 and KGd_2F_7 have been obtained from calorimetric measurements. The enthalpies have also been estimated using two correlation techniques that are independent of our measurements. The agreement between measured and predicted $\Delta_f H^0$ values is satisfactory. Therefore, the proposed estimation procedures can be used for ternary fluorides compounds when thermochemical data are not available.

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