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Enthalpies of formation from the component oxides of MgWO_4 , CaWO_4 (scheelite), SrWO_4 , and BaWO_4 , determined by high-temperature direct synthesis calorimetry

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Abstract

The enthalpies of formation, from the constituent oxides, of tungstates of alkaline earth metals, MeWO_4 (Me is Mg, Ca, Sr, Ba), have been determined by direct synthesis calorimetry at 1473 ± 2 K. The following values of ΔH_f at 298 K (kJ mol^{-1}) are reported: MgWO_4 , -73.9 ± 4.8 ; CaWO_4 (scheelite), -168.5 ± 3.3 ; SrWO_4 , -217.9 ± 3.6 ; BaWO_4 , -256.2 ± 3.9 . The results are compared with data available in the literature.

Keywords: Alkaline-earth tungstates; Enthalpy of formation; High-temperature direct synthesis calorimetry; Scheelite

1. Introduction

In the past several years, using high-temperature solute–solvent or direct synthesis calorimetry, this laboratory has successfully determined the standard enthalpies of formation of a series of binary alloys and compounds, formed either between early transition metals and late transition metals or between a wide range of transition metals and elements from Group IIIB (B, Al) and Group IVB (C, Si, Ge, Sn) in the periodic table [1–14]. Somewhat similar thermochemical studies of intermetallic compounds have been carried out previously by other laboratories, notably by the

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Laboratoire de Thermodynamique Métallurgique, Université de Nancy 1, France [15], and by the Istituto di Chimica Generale ed Inorganica, Università di Genova, Genova, Italy [16].

Recently, we have come to realize that this experimental method, which so far has been used with success only for alloys and related compounds, may also be used in studies of other refractory materials such as oxides. The thermochemistry of mixed oxide systems is of considerable importance in inorganic chemistry, in the earth sciences, and in ceramic technology. For most mixed oxide systems, the only calorimetric method used so far to obtain heats of formation is solution calorimetry, an indirect method. However, because of the difficulties associated with dissolving many oxides in aqueous solvents near room temperature, calorimetric determinations of heats of formation of mixed oxide phases by this method were always very difficult. A considerable improvement was achieved in the development of high-temperature oxide melt solution calorimetry by the senior author of this paper in the 1960s [17].

The present study represents the first known attempt to use high-temperature direct synthesis calorimetry to determine the heats of formation of mixed oxides from their component oxides. In this investigation we have determined the enthalpies of formation from the two component oxides of MgWO_4 , CaWO_4 (scheelite), SrWO_4 and BaWO_4 . The results will be compared with earlier data listed by the National Bureau of Standards [18], by Kubaschewski et al. [19], and with a value for MgWO_4 determined by high-temperature oxide melt solution calorimetry by Navrotsky and Kleppa [20].

2. Experimental and starting materials

The experiments were all carried out at 1473 ± 2 K in a single-unit differential microcalorimeter which was described earlier in some detail [21]. All experiments were conducted in air. The actual synthesis reactions were carried out in pure alumina (Al_2O_3) crucibles.

Calibration of the calorimeter was achieved by dropping pieces of 4 mm diameter pellets of high purity platinum of known mass from room temperature into the calorimeter at 1473 ± 2 K. The enthalpy of pure platinum at this temperature, $34,106 \text{ J mol}^{-1}$, was taken from Hultgren et al. [22]. The calibrations were reproducible within $\pm 1\%$.

The MgO , CaO , SrCO_3 , BaCO_3 and WO_3 used for the experiments were all puratronic grade powders with metallic purities ranging from 99.995% for SrCO_3 , to 99.997% for BaCO_3 , to 99.998% for MgO and WO_3 , and to 99.9995% for CaO . All the powders were purchased from Johnson Matthey, Alfa Aesar group. Before the samples were prepared MgO , CaO and WO_3 were fired at 1200°C , while SrCO_3 and BaCO_3 were dried at about 190°C for 24 h. The pre-treated oxide and carbonate powders were stored in a vacuum desiccator.

The samples were prepared by mixing powders of MgO , CaO , SrCO_3 , or BaCO_3 with WO_3 powder in the appropriate stoichiometric proportions. The mixed powders were then ground in an alumina mortar to ensure good mixing and to reduce the size of the particles. The final particle size was probably less than -200 mesh. The mixed

powders were pressed into 4-mm-diameter pellets. Because it was difficult to make thick pellets of the powders, several thin pellets with thickness of about 1 mm or less were made for a single sample. Since the pellets were usually quite fragile, they were placed in cylindrical platinum capsules. These capsules were prepared from 0.05-mm-thick pure platinum foil; they were closed at both ends but were not sealed by welding. Excluding the weight of the platinum capsule the average sample weighed about 200 mg. The capsuled samples were dried overnight, again at about 190°C, before use.

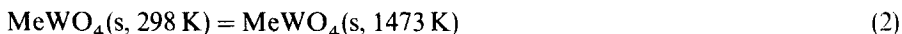
3. Experimental results

The enthalpy of formation, from the component oxides, of the compound MeWO_4 is obtained from the difference between two sets of measurements. A single measurement takes about 1 h. This is the time from the drop of the sample to when a final steady state is obtained in the calorimeter. If oxide reactants are used, in the first set of measurements the following reaction takes place in the calorimeter



Here Me stands for Mg, Ca, Sr, or Ba.

The products of reaction (1) are then re-used in a subsequent set of measurements to determine the corresponding heat contents



From Eqs. (1) and (2) we have

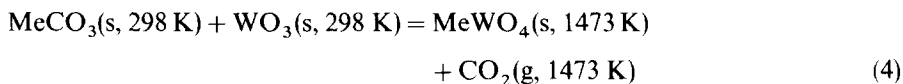


and the enthalpy of formation from the component oxides at 298 K is given by

$$\Delta H_f = \Delta H(1) - \Delta H(2)$$

where $\Delta H(1)$ and $\Delta H(2)$ are the observed enthalpy changes per mole for Eqs.(1) and (2), respectively.

Because SrO and BaO react very rapidly with water vapor and carbon dioxide in air, we chose to use SrCO_3 and BaCO_3 as starting materials rather than the oxides. When carbonates are used, the initial reaction which takes place in the calorimeter is



where Me stands for Sr or Ba. The quantity $\Delta H(1)$ can now be calculated from $\Delta H(4)$, the enthalpy change per mole for reaction (4), by calculating the enthalpy changes associated with the following two equations:



and



Clearly, we have

$$\Delta H(1) = \Delta H(4) - \Delta H(5) - \Delta H(6)$$

The values of $\Delta H(5)$ and $\Delta H(6)$, the enthalpy changes per mole for Eqs. (5) and (6), respectively, can readily be calculated from data found in the literature. The standard enthalpies of formation for SrCO_3 ($-1,218,680 \pm 725 \text{ J mol}^{-1}$), BaCO_3 ($-1,210,850 \pm 1,115 \text{ J mol}^{-1}$), and CO_2 ($-393,510 \pm 65 \text{ J mol}^{-1}$) used to calculate $\Delta H(5)$, as well as the heat content of CO_2 at 1473 K ($\Delta H(6) = 60,118 \text{ J mol}^{-1}$) were all taken from Robie et al. [23].

Table 1 summarizes all the experimental results obtained for MeWO_4 (Me is Mg, Ca, Sr, or Ba). The reported values of $\Delta H(1)$ and $\Delta H(2)$ are averages of four to eight individual determinations with standard deviations δ_1 and δ_2 , respectively. However, the δ_1 values for SrWO_4 and BaWO_4 are combinations of the standard deviations for $\Delta H(4)$ and $\Delta H(5)$. If the standard deviation for the calibration is δ_3 , the overall uncertainty in the reported enthalpy of formation is calculated from $\delta = \sqrt{\delta_1^2 + \delta_2^2 + \delta_3^2}$.

After the measurements all the samples were examined by X-ray powder diffraction. In order to detect the smallest amounts of impurities, we deliberately used unusually large samples. For this reason, the reflections of the major phase (MeWO_4) with relative intensities (I/I_1) exceeding 10 all went beyond the range of our recording chart paper. If the most intense peak of an impurity is then barely recognized in our X-ray diffraction pattern, the amount of this impurity is estimated to be of the order of 1%. Certainly, the percentage will not be over 2%. The X-ray diffraction patterns of our samples of MgWO_4 and CaWO_4 showed clear and sharp reflections which were in perfect agreement with the ASTM standard files for these two compounds. Since there was no evidence for any unreacted oxides in these two samples, the reactions between MgO or CaO and WO_3 were undoubtedly all complete. The X-ray diffraction patterns obtained from our SrWO_4 and BaWO_4 samples were also in perfect agreement with the

Table 1

Observed heats of reaction, average heat contents at 1473 K, and calculated enthalpies of formation from the component oxides (ΔH_f) and from the elements (ΔH_f^0). All data are in kJ mol^{-1} ^a

Compound	$\Delta H(1)$	$H_{1473}^0 - H_{298}^0 = \Delta H(2)$	ΔH_f	ΔH_f^0
MgWO_4	$111.08 \pm 4.30(8)$	$184.93 \pm 2.11(8)$	-73.9 ± 4.8	$-1,518.3 \pm 4.8$
CaWO_4	$13.97 \pm 2.45(4)$	$182.50 \pm 2.09(4)$	-168.5 ± 3.3	$-1,646.5 \pm 3.4$
SrWO_4	$-45.71 \pm 2.57(5)^b$	$172.23 \pm 2.48(5)$	-217.9 ± 3.6	$-1,651.3 \pm 3.7$
BaWO_4	$-80.30 \pm 3.12(5)^b$	$175.86 \pm 2.16(5)$	-256.2 ± 3.9	$-1,647.2 \pm 4.1$

^a Numbers in parentheses indicate numbers of experiments averaged.

^b $\Delta H(1)$ values for SrWO_4 and BaWO_4 were calculated from $\Delta H(4)$ values. $\Delta H(4)$ is the observed enthalpy changes for Eq. (4), which were $249.08 \pm 2.42 \text{ kJ mol}^{-1}$ (average of 5 measurements) and $249.06 \pm 2.72 \text{ kJ mol}^{-1}$ (average of 5 measurements) for SrWO_4 and BaWO_4 , respectively. $\Delta H(1) = \Delta H(4) - \Delta H(5) - \Delta H(6)$, where $\Delta H(5)$ and $\Delta H(6)$ are the enthalpy changes for Eqs. (5) and (6), respectively. The values of $\Delta H(5)$, 234.68 ± 0.86 and $269.24 \pm 1.53 \text{ kJ mol}^{-1}$ for SrWO_4 and BaWO_4 , respectively, were calculated from the standard enthalpies of formation of the carbonates and oxides, while $\Delta H(6)$ was $60.118 \text{ kJ mol}^{-1}$. These values were all taken from Robie et al. [23].

corresponding ASTM standard files, and there was no evidence for any unreacted WO_3 . However, the X-ray diffraction patterns indicated that very small amounts of SrCO_3 and BaCO_3 remained in these two samples. A possible reason why we could not detect WO_3 , but did detect SrCO_3 and BaCO_3 , may be that we found that the WO_3 powder was more readily lost during the preparation of the samples. If this occurs, we believe that the reactions between SrCO_3 or BaCO_3 and WO_3 should still be considered to be essentially complete. On the one hand, the amounts of unreacted carbonate clearly were very small; hence, they may not introduce any significant error in the reported values. On the other hand, the measured weight loss of the samples after the reactions all indicated essentially quantitative decomposition of both SrCO_3 and BaCO_3 . In fact, in all samples prepared from carbonates the weight losses actually observed were slightly larger than the values calculated assuming a complete decomposition of the carbonates. For example, our $\text{BaCO}_3 + \text{WO}_3$ sample #3 had a mass of 0.21591 g before direct synthesis, and a mass of 0.19338 g after direct synthesis, resulting in a weight loss of 0.02253 g. This sample contained 0.09925 g of BaCO_3 . Assuming a complete decomposition of BaCO_3 in this sample, the weight loss should be 0.02213 g, which is smaller than the weight loss actually observed. Thus, the extra weight loss was 0.4 mg which is 1.8% of the mass of CO_2 contained in this sample. Generally speaking, for samples based on SrCO_3 the observed weight loss was about 1.5–2.5% larger than the amount of CO_2 contained in the samples, and for samples based on BaCO_3 it was about 1–2% larger than the amount of CO_2 . Although the powders were carefully fired and/or dried at elevated temperatures before and after the sample preparations, the “extra” weight losses, which ranged from 0.1 mg to 0.6 mg for the 200 mg samples, may probably be attributed to traces of moisture trapped by the powders during sample preparation and storage. We made small corrections for this effect by taking the heat content of H_2O at 1473 K into account when we calculated the values of $\Delta H(4)$.

The above argument may be challenged by the fact that the amount of moisture (presumably H_2O) could be more than enough to compensate for some retained carbonate. To check our reported enthalpies of formation for SrWO_4 and BaWO_4 , we have calculated the enthalpy corrections for 2% unreacted carbonates in these two samples. These calculations provided new values of the enthalpies of formation from the component oxides, which were $-221.5 \pm 3.8 \text{ kJ mol}^{-1}$ for SrWO_4 and $-259.3 \pm 3.9 \text{ kJ mol}^{-1}$ for BaWO_4 , respectively. These values are consistent with our reported values in Table 1 within the stated experimental uncertainties.

In addition to the X-ray diffraction examination, the samples of CaWO_4 were also examined by scanning electron microscopy (SEM). These tests indicated that tiny euhedral single-phase crystals of CaWO_4 were formed during the direct synthesis.

4. Discussion

Fig. 1 presents a plot of all our experimental results for the enthalpies of formation from the component oxides of MeWO_4 (Me is Mg, Ca, Sr, or Ba). The earlier calorimetric value for MgWO_4 by Navrotsky and Kleppa, measured near 700°C [20], and the values for all MeWO_4 (Me is Mg, Ca, Sr, Ba) calculated from the standard

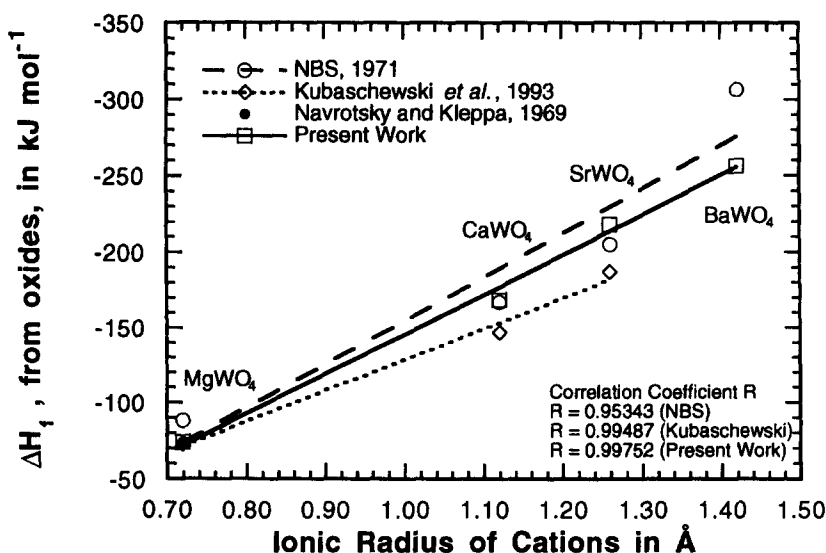


Fig. 1. The enthalpies of formation from the component oxides for MgWO_4 , CaWO_4 (scheelite), SrWO_4 and BaWO_4 plotted against the ionic radius of the divalent cations. The ionic radii (in Å, 1 Å = 100 pm) of six-fold Mg^{2+} and eight-fold Ca^{2+} , and Ba^{2+} were taken from Lide [24]. Also shown are the previous value for MgWO_4 published by Navrotsky and Kleppa [20] and the values calculated from the standard enthalpies of formation of pertinent tungstates and related oxides given by NBS [18] and by Kubaschewski et al. [19].

enthalpies of formation given by the National Bureau of Standards (NBS) [18] and by Kubaschewski et al. [19] are also shown in the figure. It is apparent that the values for MgWO_4 of Navrotsky and Kleppa ($-74.01 \pm 1.34 \text{ kJ mol}^{-1}$) and of Kubaschewski et al. ($-72.8 \pm 4.1 \text{ kJ mol}^{-1}$) are in excellent agreement with our new value ($-73.9 \pm 4.8 \text{ kJ mol}^{-1}$). However, the value for the same compound given by NBS ($-88.03 \text{ kJ mol}^{-1}$) is clearly too exothermic. Our value for CaWO_4 ($-168.5 \pm 3.3 \text{ kJ mol}^{-1}$) is very close to the corresponding value given by NBS ($-167.2 \text{ kJ mol}^{-1}$), but is significantly more exothermic than the value of Kubaschewski et al. ($-146.6 \pm 12.5 \text{ kJ mol}^{-1}$). Our enthalpy of formation for SrWO_4 ($-217.9 \pm 3.6 \text{ kJ mol}^{-1}$) is much more exothermic than the values given by NBS ($-204.8 \text{ kJ mol}^{-1}$) and by Kubaschewski et al. ($-186.6 \pm 21.0 \text{ kJ mol}^{-1}$). Kubaschewski et al. give no value for BaWO_4 . However, our new value for this compound ($-256.2 \pm 3.9 \text{ kJ mol}^{-1}$) is significantly less exothermic than that given by NBS ($-306.5 \text{ kJ mol}^{-1}$).

Also listed in Table 1 are the standard enthalpies of formation (ΔH_f°) of MgWO_4 , CaWO_4 , SrWO_4 , BaWO_4 , calculated from our measured enthalpies of formation from the component oxides (ΔH_f°) for these compounds. Table 2 presents a comparison between our ΔH_f° values and earlier values given by NBS [18] and by Kubaschewski et al. [19].

For a series of isostructural double oxides formed between a single acidic oxide, e.g., WO_3 , and a family of basic oxides formed by cations from the same group in the periodic table, it may be expected that the thermodynamic properties of the double oxides may be related to specific properties of the cations, such as the ionic radius.

Table 2

A comparison of the standard enthalpies of formation of MeWO_4 (Me is Mg, Ca, Sr, Ba) from the present work with the values from NBS [18] and from Kubaschewski et al. [19]; all data are in kJ mol^{-1}

Compound	ΔH_f° (present work)	ΔH_f° (NBS, 1982)	ΔH_f° (Kubaschewski et al., 1993)
MgWO_4	$-1,518.3 \pm 4.8$	$-1,532.6$	$-1,517.1 \pm 2.9$
CaWO_4	$-1,646.5 \pm 3.4$	$-1,645.1$	$-1,624.2 \pm 12.1$
SrWO_4	$-1,651.3 \pm 3.7$	$-1,639.7$	$-1,621.3 \pm 20.5$
BaWO_4	$-1,647.2 \pm 4.1$	$-1,702$	—

Among the double oxides considered in this paper, CaWO_4 , SrWO_4 and BaWO_4 all have the same tetragonal structure with the space group $14_1/a$, while MgWO_4 has a monoclinic structure with the space group $\text{P}2_1/a$. However, if we compare the unit cell parameters of MgWO_4 with those of CaWO_4 , SrWO_4 and BaWO_4 , it is apparent that the monoclinic structure of MgWO_4 may be considered to be a small distortion from the tetragonal structure of CaWO_4 , SrWO_4 and BaWO_4 . Therefore, it is still of interest to consider the systematic dependence of the enthalpy of formation, from the component oxides, on the ionic radius of the divalent cation. The values of the ionic radii of six-fold Mg^{2+} , and eight-fold Ca^{2+} , Sr^{2+} , and Ba^{2+} , which are 0.72, 1.12, 1.26 and 1.42 Å (1 Å = 100 pm), respectively, were taken from Lide [24]. In Fig. 1 we have fitted a straight line to our four experimental enthalpy of formation values for MeWO_4 . This line suggests a very good correlation between the ionic radius of the divalent cations and the enthalpy of formation from the component oxides. In other words, we find that the magnitude of the enthalpy of formation from the component oxides increases almost linearly with the increase of the ionic radius of the divalent cation. For comparison, we have also fitted straight lines to the values given by NBS and by Kubaschewski et al. The R values given in Fig. 1 are the correlation coefficients of the linear fittings. Obviously, the correlation coefficient for the NBS values (0.953) is inferior to that for our own values (0.998) since the NBS value for BaWO_4 is too exothermic. The R value for the data given by Kubaschewski et al. (0.995) seems roughly comparable to our own value. However, their value is not really comparable with our own because they have no value for BaWO_4 in their data.

Similar correlations for two other double oxide systems are shown in Figs. 2 and 3, in which the enthalpies of formation from the component oxides of chromates and molybdates of the alkaline earth metals are plotted against the ionic radius of the divalent cations. The data for these double oxides were all calculated from the corresponding standard enthalpies of formation of NBS [18] and of Kubaschewski et al. [19]. In both of these families of compounds we find good to excellent correlations.

High-temperature direct synthesis calorimetry may find application in other mixed oxide systems. For example, it may perhaps be used for studies of borates, vanadates, and molybdates. It may also find use in studies of some cuprates which are important in high-temperature superconductors. However, it does not apply to silicates. We carried out an exploratory experiment for CaSiO_3 at 1473 K and found that the reaction between CaO and SiO_2 at this temperature was far from complete.

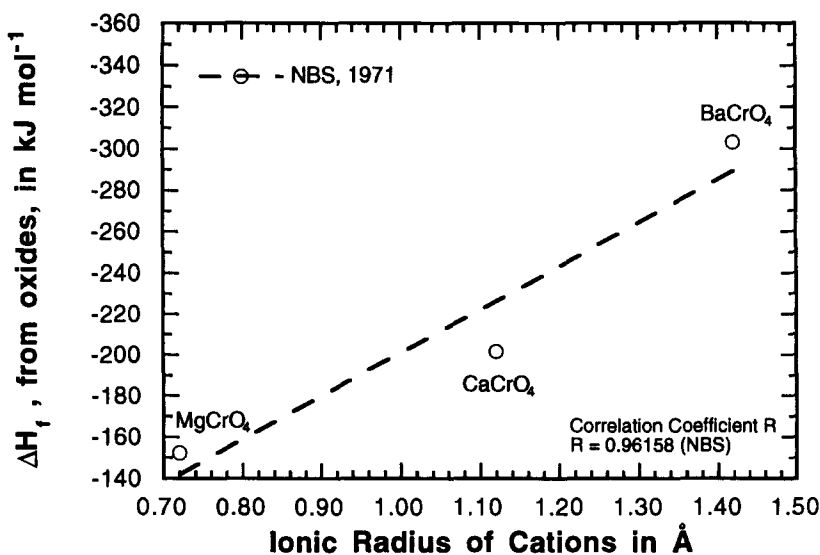


Fig. 2. The enthalpies of formation from the component oxides for MgCrO_4 , CaCrO_4 and BaCrO_4 plotted against the ionic radius of the divalent cations. The ionic radii (in $\text{\AA}$, $1 \text{\AA} = 100 \text{ pm}$) of six-fold Mg^{2+} and eight-fold Ca^{2+} , Sr^{2+} , and Ba^{2+} were taken from Lide [24]. All data were calculated from the standard enthalpies of formation of pertinent chromates and related oxides given by NBS [18].

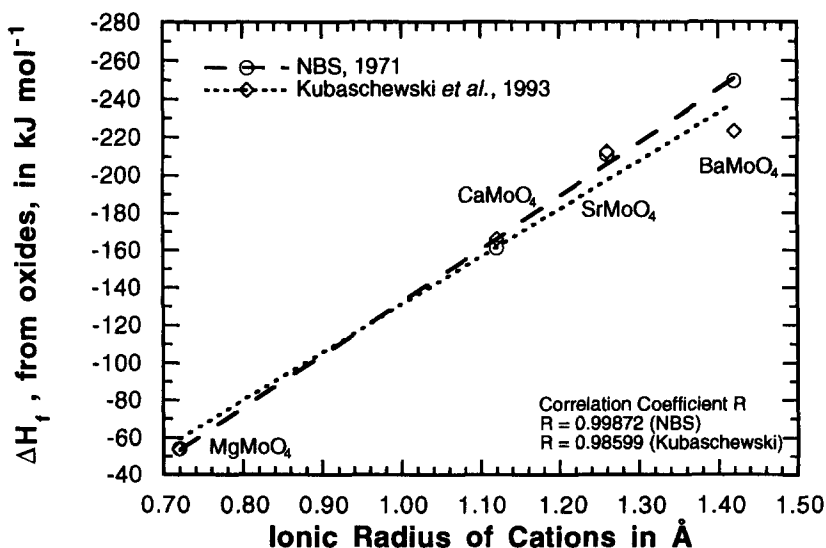


Fig. 3. The enthalpies of formation from the component oxides for MgMoO_4 , CaMoO_4 , SrMoO_4 , and BaMoO_4 plotted against the ionic radius of the divalent cations. The ionic radii (in $\text{\AA}$, $1 \text{\AA} = 100 \text{ pm}$) of six-fold Mg^{2+} and eight-fold Ca^{2+} , Sr^{2+} , and Ba^{2+} were taken from Lide [24]. All data were calculated from the standard enthalpies of formation of pertinent molybdates and related oxides given by NBS [18] and by Kubaschewski et al. [19].

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References

- [1] O.J. Kleppa, *J. Phase Equilibria*, 15 (1994) 240–263.
- [2] Q. Guo and O.J. Kleppa, *Met. Mater. Trans.*, 25B (1994) 73–77.
- [3] Q. Guo and O.J. Kleppa, *Met. Mater. Trans.*, 26B (1995) 275–279.
- [4] Q. Guo and O.J. Kleppa, *J. Alloys Comp.*, 205 (1994) 63–67.
- [5] Q. Guo and O.J. Kleppa, *J. Alloys Comp.*, 218 (1995) L21–L23.
- [6] Q. Guo and O.J. Kleppa, *J. Alloys Comp.*, 221 (1995) 45–49.
- [7] Q. Guo and O.J. Kleppa, *J. Alloys Comp.*, 221 (1995) 50–55.
- [8] Q. Guo and O.J. Kleppa, *Met. Mater. Trans.*, 27B (1996) in press.
- [9] Q. Guo and O.J. Kleppa, *J. Phys. Chem.*, 99 (1995) 2854–2856.
- [10] S.V. Meschel and O.J. Kleppa, *J. Alloys Comp.*, 217 (1995) 235–239.
- [11] S.V. Meschel and O.J. Kleppa, *J. Alloys Comp.*, 220 (1995) 88–93.
- [12] S.V. Meschel and O.J. Kleppa, *J. Alloys Comp.*, 221 (1995) 37–41.
- [13] S.V. Meschel and O.J. Kleppa, *J. Alloys Comp.*, 224 (1995) 345–350.
- [14] S.V. Meschel and O.J. Kleppa, *J. Alloys Comp.*, 227 (1995) 93–96.
- [15] J.C. Gachon, M. Notin and J. Hertz, *Assoc. Fr. Calorim. Anal. Therm. (J.C.A.T. Marseille)*, X (1979) HT2.
- [16] R. Capelli, R. Ferro and A. Borsese, *Thermochim. Acta*, 10 (1974) 13–21.
- [17] O.J. Kleppa, *Colloques internationaux du C.N.R.S.*, No. 201, *Thermochimie*, Paris C.N.R., (1972) 119–127.
- [18] D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, I. Halow, S.M. Bailey, K.L. Churney and R.L. Nuttall, *J. Phys. Chem. Ref. Data*, 11 (1982) supplement No.2.
- [19] O. Kubaschewski, C.B. Alcock and P.J. Spencer, *Materials Thermochemistry*, 6th edn., Pergamon Press, New York, 1993.
- [20] A. Navrotsky and O.J. Kleppa, *Inorg. Chem.*, 8 (1969) 756–758.
- [21] O.J. Kleppa and L. Topor, *Thermochim. Acta*, 139 (1989) 291–297.
- [22] R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, K.K. Kelley and D.D. Wagman, *Selected Values of Thermodynamic Properties of the Elements*, ASM, Metal Park, Ohio, 1973.
- [23] R.A. Robie, B.S. Hemingway and J.R. Fisher, *Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar (10^5 Pascals) Pressure and at Higher Temperatures*, U.S. Geological Survey Bulletin 1452, U.S. Government Printing Office, Washington, 1978.
- [24] D.R. Lide, *Handbook of Chemistry and Physics*, 75th edn., CRC Press, Ann Arbor, 1994.