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Heat capacities and enthalpy increments of the metazirconates of calcium, strontium and barium

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Abstract

The enthalpy increments of $CaZrO_3$(s) and $SrZrO_3$(s) have been measured by drop calorimetry from 475.6 to 845.6 K, and from 474.4 to 906.5 K, respectively. Some additional enthalpy increment measurements on $BaZrO_3$(s) have been performed from 804.3 to 899.30 K. The results are compared with other measurements on $CaZrO_3$(s), $SrZrO_3$(s) and $BaZrO_3$(s), and these are discussed critically. The heat capacity functions up to 2000 K for the three zirconates are presented.

Keywords: $BaZrO_3$; $CaZrO_3$; Enthalpy increment; Heat capacity; $SrZrO_3$

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1. Introduction

The zirconates of the alkaline-earth metals have been the subject of several investigations because of their technological applications. For instance, zirconates are used in the electronic industry as insulators, and their refractory properties are of interest in high-temperature applications. In nuclear safety studies, zirconates play an important role as they are formed in the UO_2 fuel by reaction between the fission products in the fuel matrix, and during core–concrete interactions by the reaction between the fission products and the oxidized Zircaloy cladding. The thermodynamic properties are thus of special interest as they influence the behaviour of hazardous fission products.

In this study, enthalpy-increment measurements on $CaZrO_3$(s) and $SrZrO_3$(s) have been performed, and in continuation of previous measurements [1], high-temperature enthalpy-increment measurements have been performed on $BaZrO_3$. Following a comparison of the literature data with the present measurements, their high-temperature

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behaviour is discussed and high-temperature enthalpy-increment functions up to 2000 K are given.

2. Experimental

2.1. Sample preparation

Strontium metazirconate, $SrZrO_3$, was prepared by heating stoichiometric amounts of ZrO_2 (Aldrich, Hf < 200 ppm) and $SrCO_3$ (Baker) in air at 1423 K. The starting materials were weighed in an argon-filled glove box and thoroughly mixed before being pressed into pellets. An underlying pellet of $SrZrO_3$ was used to prevent reactions with the alundum container. After the heating, the sample was ground in an alundum mortar and analysed by X-ray diffractometry (Guinier de Wolff, Cu $K\alpha_{1,2}$). The heating step was repeated until no further crystallographic changes could be observed in the sample. The X-ray pattern of the $SrZrO_3$ sample corresponds to a cubic cell with a doubled axis, as previously reported by van Roosmalen et al. [2]. Calcium metazirconate, $CaZrO_3$, was prepared similarly to $SrZrO_3$(s). As starting materials, $CaCO_3$ (Ultrex, Baker) and ZrO_2 (Cerac, Hf < 200 ppm) were used, and the maximum temperature was 1673 K. The crystal structure of the $CaZrO_3$(s) sample was entirely identical to JCPDS card number 35–0790. In a final heating, both samples were treated in purified oxygen at 973 K to compensate for possible oxygen loss during the preparation. The barium metazirconate, $BaZrO_3$, sample used in the measurements was the same as that used in the previous measurements by Cordfunke et al. [1]. Since it was not possible to analyse the samples accurately, only the molar fractions of the initial oxides are given in Table 1.

2.2. Calorimetric measurements

Enthalpy increments were measured in an isothermal diphenyl-ether drop calorimeter as described previously [3]. A sample is enclosed in a spherical quartz ampoule and heated in a furnace, the temperature of which is measured with calibrated Pt/(Pt + 10% Rh) thermocouples to 0.1 K. After a reasonable thermal equilibration time, the ampoule is dropped into the calorimeter. The energy of the ampoule plus sample now melts solid diphenyl-ether in equilibrium with its liquid in a closed system. The resulting volume increment of ether is determined by weighing the mass of the displaced mercury. The ratio of the heat input to the mass of mercury making up the volume change is a constant for the apparatus, $(79.990 \pm 0.065)\ J \cdot g^{-1}$, and is obtained

Table 1
Molar mass and composition of $AZrO_3$(s) where A is Ca, Sr, Ba

Compound	Molar mass $g\ mol^{-1}$	$nAO/nZrO_2$
$CaZrO_3$(s)	179.300	1.0001
$SrZrO_3$(s)	226.842	1.0000
$BaZrO_3$(s)	276.549	1.0001

by calibration with the NIST (formerly designated NBS) standard reference material No. 720, synthetic sapphire, Al_2O_3. The enthalpy contribution of the quartz capsule is determined separately.

For the present measurements, 5.38130 g of $CaZrO_3$ or 6.12437 g of $SrZrO_3$ were enclosed in quartz ampoules of 1.12144 g and 1.24663 g, respectively. Additional measurements on $BaZrO_3$ were performed with the same sample as in previous measurements [1]. A correction was made for the difference in enthalpy between the final calorimeter temperature (300.06 K) and the standard reference temperature (298.15 K) using the values (see below) for the heat capacities at room temperature of these zirconates determined by King and Weller [4]. All masses were corrected for buoyancy in argon.

3. Results

The high-temperature enthalpy-increment data for $CaZrO_3(s)$, $SrZrO_3(s)$ and $BaZrO_3(s)$ are given in Table 2. The high-temperature thermodynamic functions were calculated by fitting the data to a polynomial with the boundary conditions: $[H^\circ(T)-H^\circ(298.15)]=0$ at 298.15 K, and using the $C_p^\circ(298.15\text{ K})$ values obtained by King and Weller. For $CaZrO_3(s)$, we thus obtain from 298.15 to 845.6 K:

$$H^\circ(T)-H^\circ(298.15\,\mathrm{K})/\mathrm{J\,mol^{-1}}=108.6926(T/K)+12.31142\times10^{-3}(T/K)^2 \\ +14.33304\times10^{5}(T/K)^{-1}-38308.4$$

And for $SrZrO_3(s)$, we obtain from 298.15 to 906.5 K

$$H^\circ(T)-H^\circ(298.15\,\mathrm{K})/\mathrm{J\,mol^{-1}}=105.7740(T/K)+15.30911\times10^{-3}(T/K)^2 \\ +10.19858\times10^{5}(T/K)^{-1}-36318.0$$

Using the combined results of the previous [1] and the present study, we obtain for $BaZrO_3(s)$ from 298.15 to 899.3 K:

$$H^\circ(T)-H^\circ(298.15\,\mathrm{K})/\mathrm{J\,mol^{-1}}=121.7139(T/K)+3.847778\times10^{-3}(T/K)^2 \\ +19.82171\times10^{5}(T/K)^{-1}-43279.3$$

The standard deviations in the functions are about 103, 112 and 96 J mol^{-1}, respectively, in the temperature ranges given. Slightly better fit results for $CaZrO_3$ and $SrZrO_3$ could be obtained for the lowest temperatures using additional $(T/K)^n$ terms; the influence on the final result, however, is minor. The differences between measured and calculated values are also listed in Table 2.

4. Discussion

4.1. Low-temperature heat capacity and entropy

The low-temperature heat capacities of the alkaline earth zirconates of Ca, Sr and Ba have been measured by King and Weller [4] in the temperature region from 53 to 297

Table 2
Enthalpy increments of $CaZrO_3(s)$, $SrZrO_3(s)$ and $BaZrO_3(s)$

	T/(K)	$[H^\circ(T)-H^\circ(298.15\ \mathrm{K})]/(\mathrm{J\ mol^{-1}})$		δ%
		Exp.	Calc.	
$CaZrO_3$				
	475.6	19091	19184	−0.49
	521.8	24444	24506	−0.25
	567.8	29831	29901	−0.23
	614.1	35402	35417	−0.04
	660.1	40999	40975	0.06
	706.1	46820	46607	0.45
	752.4	52297	52346	−0.09
	798.6	58184	58140	0.08
	845.6	64011	64100	−0.14
$SrZrO_3(s)$				
	474.4	19313	19456	−0.74
	476.0	19505	19642	−0.70
	486.2	20804	20825	−0.10
	495.1	21737	21863	−0.58
	505.3	22981	23057	−0.33
	507.6	23161	23327	−0.71
	542.7	27493	27474	0.07
	587.4	32833	32832	−0.00
	633.8	38514	38480	0.09
	680.7	44406	44274	0.30
	726.3	50108	49986	0.24
	772.4	55947	55836	0.20
	818.3	61841	61734	0.17
	840.6	64642	64626	0.02
	865.2	67755	67836	−0.12
	906.5	73125	73271	−0.20
$BaZrO_3(s)$				
	804.30	59464	59569	−0.18
	835.70	63489	63496	−0.01
	867.40	67453	67475	−0.03
	899.30	71425	71493	−0.10

K. A recalculation of their measurements and their low-temperature estimates in the temperature region below 53 K, yielded the same results within the limits of uncertainty. Therefore, their results are adopted here

$$C_p^\circ(\mathrm{CaZrO_3(s)},\ 298.15\ \mathrm{K}) = (99.91 \pm 0.30)\ \mathrm{J\ mol^{-1}\ K^{-1}}$$

$$C_p^\circ(\mathrm{SrZrO_3(s)},\ 298.15\ \mathrm{K}) = (103.43 \pm 0.31)\ \mathrm{J\ mol^{-1}\ K^{-1}}$$

$$C_p^\circ(\mathrm{BaZrO_3(s)},\ 298.15\ \mathrm{K}) = (101.71 \pm 0.31)\ \mathrm{J\ mol^{-1}\ K^{-1}}$$

The derived entropies at room temperature are

$S°(\mathrm{CaZrO_3(s)}, 298.15\ \mathrm{K}) = (100.00 \pm 0.84)\ \mathrm{J\ mol^{-1}\ K^{-1}}$

$S°(\mathrm{SrZrO_3(s)}, 298.15\ \mathrm{K}) = (115.06 \pm 0.84)\ \mathrm{J\ mol^{-1}\ K^{-1}}$

$S°(\mathrm{BaZrO_3(s)}, 298.15\ \mathrm{K}) = (124.68 \pm 1.26)\ \mathrm{J\ mol^{-1}\ K^{-1}}$

It is remarkable that at room temperature the numerical value for the heat capacity of strontium zirconate is higher than that for barium zirconate, whereas the entropies show the normal, i.e. expected, order. It can be seen in Fig. 1 that up to 100 K there is 'normal' behaviour for all three. At higher temperatures, the heat capacity increment of barium zirconate decreases, finally resulting in a lower heat capacity at 298.15 K.

4.2. *High-temperature enthalpy increments*

$CaZrO_3(s)$: For the high-temperature enthalpy increment of $CaZrO_3(s)$, four series of measurements exist, by Mezaki et al. [5], Gvelesiani et al. [6], Saha et al. [7], and Gospodinov and Marchev [8]. Their relationship with the low-temperature heat-capacity measurements of King and Weller is given in Fig. 2 as the reduced enthalpy increment. The measurements by Mezaki et al. show no smooth fit with the low-temperature data and are definitely too high. Gvelesiani's measurements show a good agreement with the low-temperature heat capacity measurements of Weller and King. The measurements by Saha et al. suggest a much steeper increment function in the temperature region between 298.15 and 1000 K, whereas the measurements of Gos-

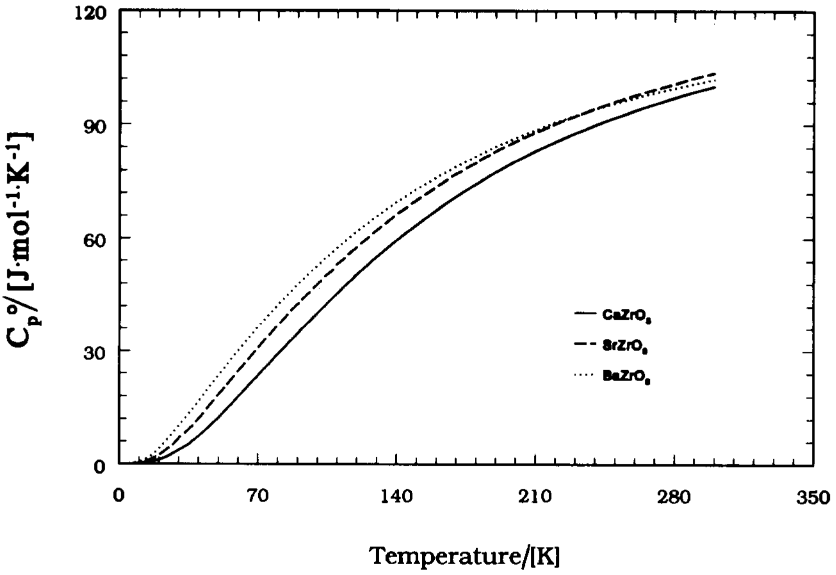

Fig. 1. The low-temperature heat capacity of $AZrO_3(s)$, and A = Ca, Sr, Ba, according to King and Weller [4].

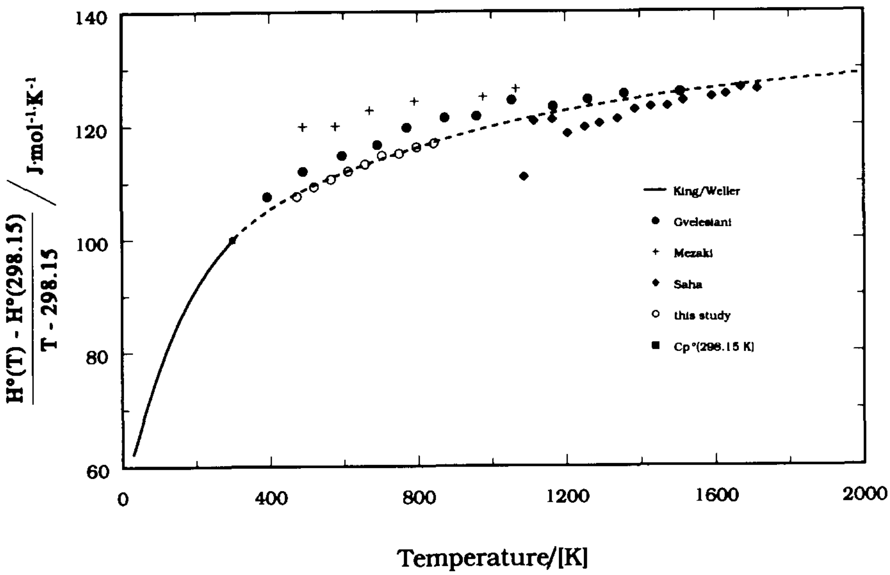

Fig. 2. The reduced enthalpy increment of $CaZrO_3(s)$.

podinov and Marchev do not even fit the scale of the figure. The latter set of data has therefore been disregarded.

The new measurements presented in this study show a good smooth fit with the low-temperature data of King and Weller. Nevertheless, the results differ considerably from those obtained by Gvelesiani et al. Extrapolation outside the temperature region in which the measurements were performed results in an enthalpy increment of the given function which becomes too large. However, on the basis of the reported structural similarity of the alkaline earth metazirconates above 1873 K [9] and using the high-temperature trends of the measurements of Gvelesiani et al. and Saha et al., the following function has been calculated for the temperature region above 845.6 K

$$H^\circ(T) - H^\circ(298.15\,\mathrm{K})/\mathrm{J\,mol^{-1}} = 139.9242(T/K) - 3.954569 \times 10^{-9}(T/K)^2 + 88.77250 \times 10^5 (T/K)^{-1} - 64717.9$$

$SrZrO_3(s)$: The high-temperature functions of $SrZrO_3(s)$ have been measured by several authors: Gospodinov and Marchev [8], Fomichev et al. [10], Levitskii et al. [11], and Nagarajan et al. [12]. The results obtained in these studies do not agree, as can be seen in Fig. 3.

The most likely explanation for these differences is the purity of the samples, and small differences in the crystal structures. $SrZrO_3(s)$ is reported to have crystal structures varying from cubic to orthorhombic. Only recently, Van Roosmalen [2] indicated that 'true' $SrZrO_3$ is cubic, but that the crystal structure is very sensitive to lattice defects caused by impurities or too high preparation temperatures, finally resulting in a distortion of the perovskite structure.

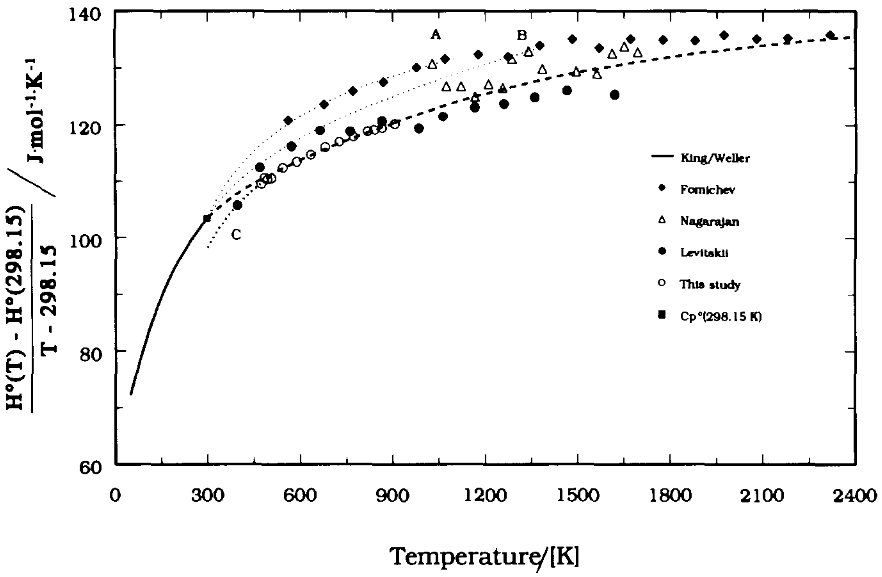

Fig. 3. The reduced enthalpy increment of $SrZrO_3(s)$: A, orthorhombic; B, tetragonal; and C, the most favourable extrapolated enthalpy-increment function of the cubic structure.

Fomichev et al. [10] and Nagarajan et al. [12] did not report the crystal structure of their samples. In view of the preparation temperatures of 1750 and 1373 K, respectively, they are probably orthorhombic and tetragonal. The sample of Levitskii et al. [11] was tetragonal. The measurements by Gospodinov and Marchev [8] will be disregarded altogether since these have no physical meaning. In Fig. 3, the possible influence of the crystal structure on the reduced enthalpy increment can be seen. The dotted curves A and B indicate an enthalpy increment function of the orthorhombic and the tetragonal structure, respectively. It is evident that the higher the crystallographic symmetry of the sample the lower the enthalpy increment of $SrZrO_3(s)$ becomes. This is in agreement with the present measurements in which care was taken to use a cubic sample.

As shown in Fig. 3, most of the high-temperature enthalpy increment series join the low-temperature heat-capacity measurements of King and Weller [4]. The crystallographic structure and purity of the sample used by these authors is not described very clearly, whereas the preparation temperature of their sample is not in agreement with the fact that they report it to have a cubic structure. Moreover, they refer to an NBS Circular [13], in which only orthorhombic strontium zirconate is mentioned. In view of the preparation temperature (1743 K), it seems most likely that their sample was orthorhombic. This could be an explanation for the remarkable low-temperature heat-capacity behaviour of this compound compared to $BaZrO_3$. Fig. 3 (curve C) shows the extrapolated enthalpy increment function based on the present measurements, indicating a significantly lower heat capacity and entropy at 298.15 K than observed by King and Weller. Extrapolation of this function to above 906.5 K is not recommended. Due to the high boundary condition for the heat capacity at room-temperature, the curvature of the function is too small and, consequently, the enthalpy-increment above 906.5 K becomes too large. Since all other high-temperature enthalpy increment measurements on strontium zirconate have been performed on non-cubic structures, the temperature function for the 'true' cubic phase above 906.5 K is unknown. However, on the basis of structural similarity with calcium and barium zirconate, the following function has been estimated for the temperature range above 906.5 K:

$$H^\circ(T) - H^\circ(298.15\,\mathrm{K})/\mathrm{J\,mol^{-1}} = 147.4092(T/K) - 7.541551\times 10^{-7}(T/K)^2 + 1.242432\times 10^{7}(T/K)^{-1} - 74060.3$$

$BaZrO_3(s)$: Unlike $SrZrO_3(s)$, there is more agreement between the high-temperature functions of $BaZrO_3(s)$. Four series of measurements are available (Fig. 4): Gospodinov and Marchev [8], Fomichev et al. [10], Nagarajan et al. [12], and Cordfunke and Konings [1]. In addition to the results of the latter authors, some measurements at higher temperatures have been performed (Table 2). Again, the measurements of Gospodinov are disregarded. Fomichev et al. found two phase transitions; high-temperature crystallographic measurements by Mathews et al. [14] revealed, however, no phase transitions. The measurements by Nagarajan et al., over almost their entire temperature region, are lower than our extrapolated high-temperature enthalpy increment function, the differences with the function derived in the present study being 2–3.5%. In a subsequent discussion, Nagarajan [15] pointed out

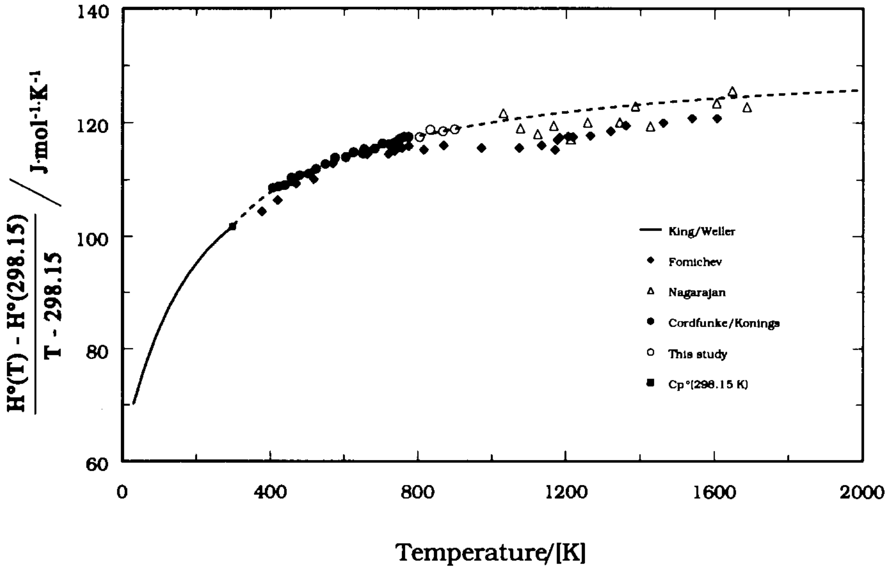

Fig. 4. The reduced enthalpy increment of $BaZrO_3(s)$.

that on the basis of the measurements by Cordfunke and Konings [1] their measurements could not be rejected. However, since the drop-calorimetric measurements performed at our Institute typically have an uncertainty of 0.4%, their results deviate significantly. This is substantiated by the additional measurements performed in the present study. Therefore, the combined set of Cordfunke and Konings [1] and the present study is adopted here. In the temperature range beyond our measurements, the enthalpy increment functions have been adopted to follow the trends measured by Fomichev et al. and Nagarajan et al. Therefore, the recommended function above 899.3 K is:

$$H^\circ(T)-H^\circ(298.15\,\mathrm{K})/\mathrm{J\,mol^{-1}} = 132.0975(T/K) - 9.909065\times10^{-3}(T/K)^2$$
$$+\,47.81382\times10^{5}(T/K)^{-1} - 52617.2$$

For completeness, the enthalpy increment functions of the alkaline earth zirconates are given in Table 3 and the reduced enthalpy increment functions are shown in Fig. 5. The high-temperature order of the heat capacity, namely, $SrZrO_3 > CaZrO_3 > BaZrO_3$, needs some further explanation. The crystallographic structure of barium zirconate at room temperature is nearly that of an ideal perovskite, whereas the structures of calcium and strontium zirconate are those of a distorted perovskite. As can be seen in Fig. 3, there is a distinct influence of the structure on the enthalpy increment function: the lower the symmetry, the higher the enthalpy increment. The higher enthalpy increment of calcium and strontium zirconate compared to barium zirconate can be explained by this effect. Although strontium zirconate is reported to be cubic, the heat capacity in the end is still larger than (orthorhombic) calcium zirconate, probably because of the fact that $SrZrO_3$ is under much more stress and wiggles between being cubic and orthorhombic [2]. At still higher temperatures, all three zirconates are reported to attain the same cubic structure [9,14]. Nevertheless, the order in the heat capacities still remains unexpected. This suggests that, besides the influence of the structure, other phenomena have to be accounted for as well. The

Table 3
The recommended high-temperature enthalpy-increment coefficients for $AZrO_3$(s) where A is Ca, Sr, Ba in the temperature range $T = 298.15$–$2000\,\mathrm{K}$

Compound	Temperature region T/K	Coefficients $H^\circ(T)-H^\circ(298.15\,\mathrm{K})/\mathrm{kJ\,mol^{-1}} = AT + BT^2 + CT^{-1} + D$			
		A	B	C	D
$CaZrO_3$	298.15 – 845.6	108.6926	1.231142×10^{-2}	14.33304×10^{5}	−38308.4
	845.6 – 2000.0	139.9242	-3.954569×10^{-9}	88.77250×10^{5}	−64717.9
$SrZrO_3$	298.15 – 906.5	105.7740	1.530911×10^{-2}	10.19858×10^{5}	−36318.0
	906.5 – 2000.0	147.4092	-7.541551×10^{-7}	12.42432×10^{6}	−74060.3
$BaZrO_3$	298.15 – 899.3	121.7139	3.847778×10^{-3}	19.82171×10^{5}	−43279.3
	899.3 – 2000.0	132.0975	-9.909065×10^{-7}	47.81382×10^{5}	−52617.2

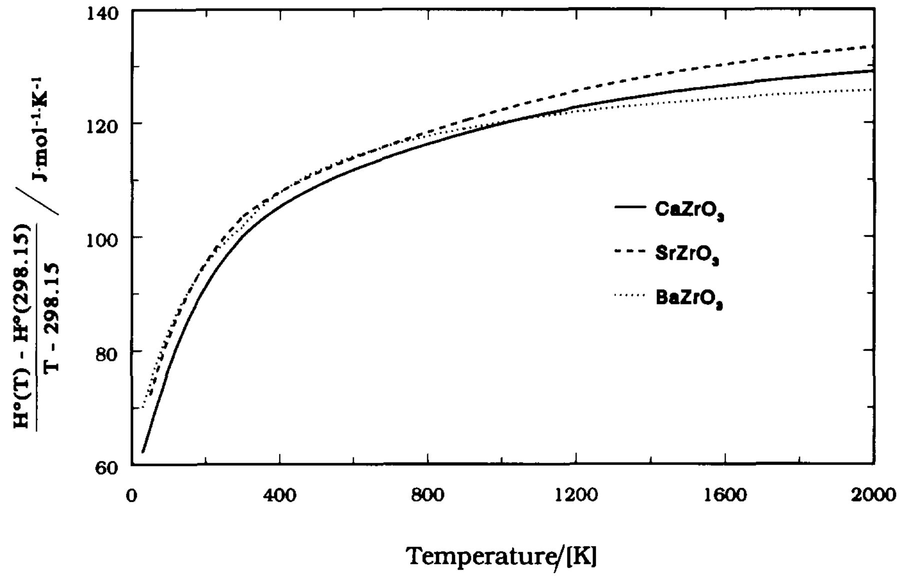

Fig. 5. A graphical representation of the recommended enthalpy-increment function of $AZrO_3(s)$, where A is Ca, Sr, Ba.

explanation of this can only be given if (new) accurate high-temperature enthalpy-increment measurements (> 1500 K) are performed.

The calculated functions are continuously monotone in both enthalpy increment and heat capacity, and can be extrapolated beyond the temperature limit given, if necessary.

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References

[1] E.H.P. Cordfunke and R.J.M. Konings, Thermochim. Acta, 156 (1989) 45.
[2] J.A.M. van Roosmalen, P. van Vlaanderen and E.H.P. Cordfunke, J. Solid State Chem., 101 (1992) 59.
[3] E.H.P. Cordfunke, R.P. Muis and G Prins, J. Chem. Thermodyn., 11 (1979) 819.
[4] E.G. King and W.W. Weller, Report BMI 5571 (1960).
[5] R. Mezaki, E.W. Tilleux, T.F. Jambois and J.L. Margrave, Adv. Thermophys. Prop. Extreme Temp. Press., 3rd ASME Symp., Lafayette, Indiana, 1965, p. 138.
[6] G.G. Gvelesiani, D.S. Tsagareishvili, I.S. Omiadza, V.A. Levitskii and P.B. Narchuk, Inorg. Mater., 18 (1982) 991.
[7] R. Saha, R. Babu, K. Nagarajan and C.K. Mathews, J. Nucl. Mater., 167 (1989) 271.
[8] G.G. Gospodinov and V.M. Marchev, Thermochim. Acta, 222 (1993) 137.

[9] M. Foëx, J.P. Traverse and J. Coutures, C.R. Acad. Sci. Paris, Series C (1967) 1837.
[10] E.N. Fomichev, N.P. Slyusar, A.D. Krivorontenko and V.Ya Tolstaya, Ognuepory, 7 (1973) 36 (Engl. transl. 7, 432).
[11] V.A. Levitskii, D.Sh. Tsagareishvili and G.G. Gveleiani, Teploviz. Vys. Temp., 14 (1976) 78 (High Temp., 14, 69).
[12] K. Nagarajan, R. Saha, R. Babu and C.K. Mathews, Thermochim. Acta, 90 (1985) 297.
[13] H.E. Swanson, M.I. Cook, T. Isaacs and E.H. Evans, NBS Circular 539, 9 (1960) 51.
[14] M.D. Mathews, E.B. Mirza and A.C. Momin, J. Mater. Sci. Lett., 10 (1991) 305.
[15] K. Nagarajan, R. Babu and C.K. Mathews, Thermochim. Acta, 179 (1991) 337.