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Estimation of thermochemical properties for ceramic oxides: a focus on $PbZrO_3$

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Abstract

Accurate standard-state thermochemical data are necessary for the quantitative modeling of the synthesis of ceramic materials and other natural or industrial processes. In some cases, such data are not available from experimental measurements in the whole temperature range of interest. Therefore, techniques have been established for the prediction of standard-state Gibbs energies, entropies and heat capacities of perovskite-type crystalline solids. These techniques are based on linear relationships between the thermochemical properties of selected families of multicomponent oxides and those of constituent groups or simple oxides. In this way, accurate empirical correlations have been developed. These correlations have been utilized to predict the standard-state properties of lead zirconate, which are not known from experiment at temperatures below 800 K.

Keywords: Estimation; Group contribution; Lead zirconate; Perovskite; Standard-state

1. Introduction

Accurate standard-state thermochemical properties, i.e., the Gibbs energy and enthalpy of formation as well as entropy, heat capacity and molar volume, are prerequisites for the modeling of chemical and phase equilibria in natural and

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industrial systems. In particular, it was shown in recent papers [1–4] that the hydrothermal synthesis of various ceramic materials such as $BaTiO_3$, $SrTiO_3$, $PbTiO_3$, $CaTiO_3$, etc. can be quantatively modeled if the thermochemical properties are accurately known. In many cases, however, these properties are not available from experimental measurements and have to be estimated. In this study, we develop empirical procedures for calculating the standard-state thermochemical properties of perovskite-type multicomponent oxides of the general formula $Me^{II}Me^{IV}O_3$ (Me^{II} is Ca, Sr, Ba, Pb, etc.; Me^{IV} is Ti, Zr, etc.). These materials are used for a variety of applications such as dielectric ceramics for capacitors, piezoelectric materials for transducers and sensors, electrostrictive ceramics for actuator devices and micropositioners, and transparent electrooptic ceramics for information storage and optical signal processing [5]. We focus on lead zirconate ($PbZrO_3$) as an example of a compound, for which thermochemical tables are not available and no experiments have been performed below 800 K. This compound is important for practical applications as an end member of the solid solution with lead titanate ($PbZr_xTi_{1-x}O_3$).

2. Gibbs energy

Various methods for the estimation of the Gibbs energy have been reviewed by Nordstrom and Munoz [6]. Most methods used for predicting the Gibbs energies and enthalpies of crystalline solids [7–10] introduce uncertainties of about $\pm(20-40)$ kJ mol^{-1}, which are typically too large for modeling hydrothermal systems. Recently, Sverjensky [7,8] proposed to correlate the standard Gibbs energies of formation of an isostructural family of crystalline solids with those of aqueous cations of a given charge. Because he restricted the analysis to carefully selected compound families, e.g., carbonates with calcite structure, oxides with the NaCl structure, ferrite spinels, etc., he was able to obtain considerably smaller deviations of about 1–4 kJ mol^{-1}. It was shown that a strong linear correlation exists between the Gibbs energy of formation of solids ($\Delta_f G^\ominus$(MeZ, cr)) and that of aqueous divalent cations ($\Delta_f G^\ominus(Me^{2+}$, ao)) at 298.15 K and 1 bar

$$\Delta_f G^\ominus(\mathrm{MeZ,\ cr}) = a_Z\,\Delta_f G^\ominus(\mathrm{Me}^{2+},\ \mathrm{ao}) + b_Z \qquad (1)$$

where Z is a divalent anion (mono- or polyatomic) that forms a salt with Me^{2+}, and the constants a_Z and b_Z depend on the anion Z. In other studies [9,10], Sverjensky also used the cation radius as an indpendent variable for correlations.

The family analysis is perfectly suited for the analysis of perovskite-type multicomponent oxides. Fig. 1 shows the linear correlations between $\Delta_f G^\ominus$(MeZ, cr) and $\Delta_f G^\ominus(Me^{2+}$, ao) for $Z = TiO_3^{2-}$, SiO_3^{2-}, ZrO_3^{2-}, SeO_3^{2-}, WO_4^{2-}, $Al_2O_4^{2-}$ and $Fe_2O_4^{2-}$ at 298.15 K. For each family, a good linear correlation is obtained. A slight deviation from linearity is noted only for Ca^{2+}, Sr^{2+} and Ba^{2+} as the Me^{2+} cations. Moreover, the lines for each family are parallel to each other. Although the line for zirconates is anchored only at three experimental points, we can assume that it is also parallel to the other lines. It should be noted that other families of

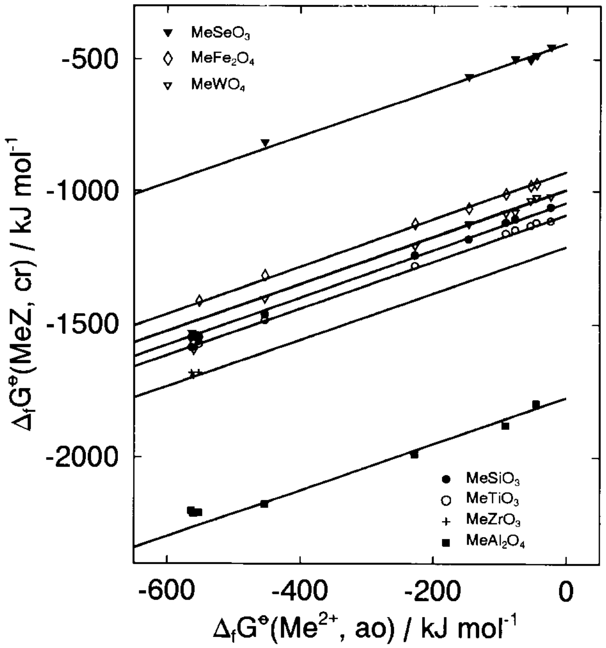

Fig. 1. Linear relationship between the Gibbs energies of formation for multicomponent oxide families (MeZ) and divalent metal cations (Me^{2+}).

compounds can be found for which linear correlations exist, e.g., Me_2TiO_4 and Me_2SiO_4, but the lines are not parallel to those shown in Fig. 1. However, Fig. 1 shows that there is every indication that the lines for the perovskite titanates and zirconates ($MeTiO_3$ and $MeZrO_3$) as well as the other families should be parallel.

This analysis has been performed using experimental data from the compilation of Barin [11], which is the most comprehensive collection of thermochemical data for solids. Barin's data for the majority of the examined compounds agree with those from other compilations [12–15]. The data for the Gibbs energy of formation of the divalent cations have been taken from the paper of Shock and Helgeson [16]. The coefficient a_z for the compounds shown in Fig. 1 is 0.87500. The coefficients b_z for the separate families are collected in Table 1 along with the relative average absolute deviations of the linear fits. The Gibbs energy of formation for $PbZrO_3$ is then estimated at

$$\Delta_f G^\ominus(PbZrO_3, \text{cr}, 298.15) = -1230.0 \text{ kJ mol}^{-1} \qquad (2)$$

Although no experimental data exist for $\Delta_f G^\ominus(PbZrO_3, \text{cr})$ at 298.15 K, the plausibility of the estimated value can be assessed using the available data for high-temperature systems. Jacob and Shim [17] determined the Gibbs energy of formation of $PbZrO_3$ from oxides by electrochemical measurements on solid state cells from 800 to 1130 K. Their result for the stoichiometric compound $PbZrO_3$ is

Table 1
Coefficients b_z and relative average absolute deviations AAD in Eq. (1) for the various families of multicomponent oxides MeZ

Z	b_z	AAD[a]
TiO_3^{2-}	−1085.0	0.0044
SiO_3^{2-}	−1047.0	0.0070
ZrO_3^{2-}	−1209.1	0.0074
SeO_3^{2-}	−434.8	0.0165
WO_4^{2-}	−1001.5	0.0089
$Al_2O_4^{2-}$	−1773.0	0.0153
$F_2O_4^{2-}$	−929.7	0.0041

[a] $\mathrm{AAD} = (1/n)\Sigma_{i=1}^{n} \left|1 - \Delta_f G_i^\ominus \text{ (calc)}/\Delta_f G_i^\ominus \text{ (exp)}\right|$; n is the number of compounds in a family.

$$\Delta_r G^\ominus(\mathrm{PbO(cr,\ massicot)} + \mathrm{ZrO_2(cr,\ monoclinic)} \rightarrow \mathrm{PbZrO_3(cr,\ cubic)}) \\ = -5.020 - 7.47 \times 10^{-3} T \ \mathrm{kJ\ mol^{-1}} \tag{3}$$

Subsequently, the Gibbs energy of formation from elements at 298.15 K can be calculated from an extrapolated value of the Gibbs energy of formation for oxides and the Gibbs energy of formation of solid PbO and ZrO_2, which are very well known [11]

$$\Delta_f G^\ominus(\mathrm{PbZrO_3,\ cr}) = \Delta_r G^\ominus(\mathrm{PbO(cr,\ massicot)} \\ + \mathrm{ZrO_2(cr,\ monoclinic)} \rightarrow \mathrm{PbZrO_3(cr,\ cubic)}) \\ + \Delta_f G^\ominus(\mathrm{PbO,\ cr}) + \Delta_f G^\ominus(\mathrm{ZrO_2,\ cr}) \tag{4}$$

At 298.15 K, the Gibbs energy of formation of $PbZrO_3$ from elements is then equal to $\Delta_f G^\ominus(\mathrm{PbZrO_3,\ cr}) = -1235.6\ \mathrm{kJ\ mol^{-1}}$, which is in excellent agreement with that obtained from the compound family analysis.

Because this agreement may be fortuitous, we also calculated the Gibbs energy of formation of $PbZrO_3$ from oxides from the high-temperature vapor pressure measurements of Härdtl and Rau [18] and Holman and Fulrath [19]. Because PbO is the only volatile species in the system $PbO + ZrO_2$, the Gibbs energy change for the reaction

$$\mathrm{PbO(cr,\ massicot)} + \mathrm{ZrO_2(cr)} \rightarrow \mathrm{PbZrO_3(cr)} \tag{5}$$

can be calculated as

$$\Delta_r G^\ominus(\mathrm{PbO(cr,\ massicot)} + \mathrm{ZrO_2(cr)} \rightarrow \mathrm{PbZrO_3(cr)}) \\ = RT \ln[P_{\mathrm{PbO(PbZrO_3)}}/P_{\mathrm{PbO(PbO)}}] \tag{6}$$

where $P_{\mathrm{PbO(PbZrO_3)}}$ and $P_{\mathrm{PbO(PbO)}}$ are the vapor pressures of monomeric PbO over solid $PbZrO_3$ and PbO, respectively. Shim and Jacob [17,20] recognized that the PbO vapor contains several associated species (monomer through hexamer) whose presence affects the total equilibrium pressure. The equilibrium constants for the formation of multimers are available from the mass spectrometric data of Drowart

Table 2
Temperature dependence of the equilibrium constants K_0 and K_n in Eq. (7)

Constant	$-RT \ln K_i$	Constant	$-RT \ln K_i$
K_0	$122610-35.83T$	K_4	$823335-446.23T$
K_2	$259199-136.40T$	K_5	$1059180-596.60T$
K_3	$512856-280.73T$	K_6	$1347350-747.80T$

et al. [21]. By solving material balance and chemical equilibrium expressions, Shim and Jacob [17,20] derived an equation that relates the total pressure of multimeric PbO(P_T) to the pressure of monomeric PbO(P_{PbO})

$$P_T = (\sqrt{2}\ K_0 P_{PbO})^{2/3}(M_{Pb} M_{O_2}^{-1})^{1/6} M_{PbO}^{(-1/2)}[M_{Pb}^{1/2} + M_{O_2}/2M_{Pb}^{1/2}] + \sum_{n=1}^{6} n^{1/2}(P_{PbO})^n/K_n \tag{7}$$

where K_0 is the equilibrium constant for the reaction $PbO(g) \rightarrow Pb(g) + 0.5O_2(g)$, $K_n (n = 2, \ldots, 6)$ are the equilibrium constants for the reactions $(PbO)_n(g) \rightarrow nPbO(g)$ and M_{Pb}, M_{O_2}, and M_{PbO} are the molecular weights of Pb, O_2, and PbO, respectively. Expressions for the constants K_0 and K_n are collected in Table 2.

From the measurements of Härdtl and Rau [18], the total vapor pressure of multimeric PbO over $PbZrO_3$ is

$$\log P_{T,PbO(PbZrO_3)} = -13660/T + 7.15 \quad 1100 < T < 1265, \quad T \text{ in K}, \ P \text{ in atm.} \tag{8}$$

The total vapor pressure of PbO over solid PbO is

$$\log P_{T,PbO(PbO)} = -15030/T + 9.51 \quad 1025 < T < 1176, \quad T \text{ in K}, \ P \text{ in atm.} \tag{9}$$

The pressures of monomeric PbO are calculated by substituting the values of $P_{T,PbO(PbZrO_3)}$ and $P_{T,PbO(PbO)}$ from Eqs. (8) and (9) into Eq. (7) and solving Eq. (7) numerically with respect to $P_{PbO(PbZrO_3)}$ and $P_{PbO(PbO)}$. Subsequently, the values of $P_{PbO(PbZrO_3)}$ and $P_{PbO(PbO)}$ were substituted into Eq. (6) to calculate the Gibbs energy of formation from oxides. The obtained values of the Gibbs energy of reaction (5) lie on a straight line given by the equation

$$\Delta_r G^\ominus(\text{PbO(cr, massicot)} + ZrO_2(\text{cr}) \rightarrow PbZrO_3(\text{cr})) = 13.160 - 21.43 \times 10^{-3}\ T \text{ kJ mol}^{-1} \tag{10}$$

Using Eq. (10) we can estimate $\Delta_f G^\ominus(PbZrO_3$, cr, 298.15 K) at -1221.5 kJ mol^{-1}. This value is somewhat different (by about 0.7%) from the value obtained from compound family analysis, but some deviation is unavoidable in view of the extrapolation of the high-temperature data.

To assess the reliability of the temperature extrapolation, it is worthwhile to compare the enthalpies of formation calculated from Eqs. (3) and (10) with the enthalpy determined calorimetrically by Takayama-Muromachi and Navrotsky [22]. The experimental value is

$$\Delta_r H^{\ominus}(\mathrm{PbO}(\text{massicot, cr}) + \mathrm{ZrO_2}(\text{monoclinic, cr}) \rightarrow \mathrm{PbZrO_3}(\text{cr}), 1068)$$
$$= 1.7 \pm 6.6 \text{ kJ mol}^{-1} \tag{11}$$

whereas the values obtained from Eqs. (3) and (10) are $-5.020(\pm 2.000)$ [17] and 13.160 kJ mol^{-1}, respectively. It is evident that only the value of the enthalpy of formation from electrochemical measurements lies within the confidence interval of Takayama-Muromachi and Navrotsky's measurements. Therefore, Eq. (3) can be assumed to be more plausible and its extrapolation to lower temperatures should be more reliable. Not unexpectedly, the $\Delta_f G^{\ominus}(\mathrm{PbZrO_3}$, cr, 298.15) value extrapolated from the electrochemical measurements, i.e., 1235.6 kJ mol^{-1}, is in a better agreement with our estimate (-1230.0 kJ mol^{-1}) than the value extrapolated from vapor data (-1221.5 kJ mol^{-1}).

3. Entropy

Several empirical methods [23–29,6] have been proposed for the estimation of entropies. Here, we utilize the methods that are applicable to the families of perovskite-type ceramics. In the first method, due to Latimer [24], the entropy is estimated from a sum of valence-dependent ionic contributions into the solid. Fig. 2 illustrates the accuracy of this method for several titanates and zirconates ($\mathrm{Me^{II}Me^{IV}O_3}$). The relative average absolute deviation for all compounds is 0.0527. When applied to $\mathrm{PbZrO_3}$, the method yields

$$S^{\ominus}(\mathrm{PbZrO_3}, \mathrm{cr}) = S^{\ominus}(\mathrm{Pb}) + S^{\ominus}(\mathrm{Zr}) + S^{\ominus}(\mathrm{O_{II}^{2-}}) + 2S^{\ominus}(\mathrm{O_{IV}^{2-}})$$
$$= 125.9 \text{ J mol}^{-1} \text{ K}^{-1} \tag{12}$$

where $S^{\ominus}(\mathrm{O_{II}^{2-}})$ and $S^{\ominus}(\mathrm{O_{IV}^{2-}})$ are contributions for oxygen attached to $\mathrm{Me^{II}}$ and $\mathrm{Me^{IV}}$, respectively.

Alternatively, the entropy of a compound $\mathrm{Me^{II}Me^{IV}O_3}$ can be calculated using the entropy of constituent oxides $\mathrm{Me^{II}O}$ and $\mathrm{Me^{IV}O_2}$. We established a linear relationship between the sum of entropies of the constituent oxides and the entropy of zirconates ($\mathrm{MeZrO_3}$) and titanates ($\mathrm{MeTiO_3}$). This relationship is illustrated in Fig. 3 and makes it possible to determine the entropy of other compounds that have not been experimentally investigated. The lines in Fig. 3 are represented by the equations

$$S^{\ominus}(\mathrm{MeZ}, \mathrm{cr}) = 0.800 \sum S^{\ominus}(\text{oxides, cr}) + 29.0 \quad \text{J mol}^{-1}\text{ K}^{-1} \text{ for zirconates} \tag{13a}$$

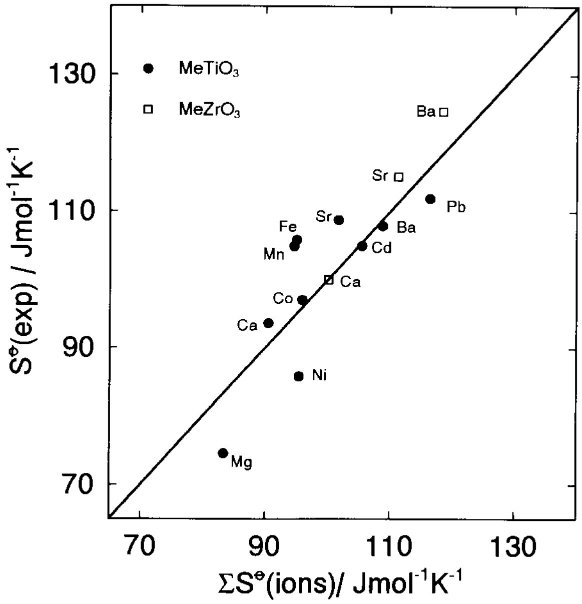

Fig. 2. Prediction of entropy from valence-dependent ionic contributions for metal titanates and zirconates.

$$S^{\ominus}(\mathrm{MeZ, cr}) = 0.800 \sum S^{\ominus}(\mathrm{oxides, cr}) + 18.0 \quad \mathrm{J\ mol^{-1}\ K^{-1}\ for\ titanates} \tag{13b}$$

The lines for zirconates and titanates are parallel to each other. The relative average absolute deviations for zirconates and titanates are 0.0077 and 0.0364, respectively. It should be noted that the entropy value for PbO was chosen to be that of its massicot structural form. This method has, in general, similar accuracy to the ionic contribution method. When applied to $PbZrO_3$, the method yields

$$S^{\ominus}(\mathrm{PbZrO_3, cr}) = 124.2\ \mathrm{J\ mol^{-1}\ K^{-1}} \tag{14}$$

Fyfe et al. [27] and, subsequently, Holland [25] used the differences between entropies and molar volumes ($S^{\ominus} - V^{\ominus}$) for oxides to estimate entropies of more complex compounds according to the group contribution formula

$$(S^{\ominus} - kV^{\ominus})(\mathrm{MeZ, cr}) = \sum n_i (S_i^{\ominus} - kV_i^{\ominus}) \tag{15}$$

where n_i is the number of constituent oxides units of type i in a molecule of a complex compound, and k is an arbitrary constant determined from measurements. According to Holland [25], k is approximately 1.0 if the units of the entropy are in J mol^{-1} K^{-1} and volumes are in cm^3 mol^{-1}. In the case of zirconates and titanates for which experimental data exist, it was determined that the straightforward summation of the ($S_i^{\ominus} - V_i^{\ominus}$) contributions leads to somewhat less accurate results than the summation of $S_i^{\ominus}$ contributions for ions or constituent oxides. However,

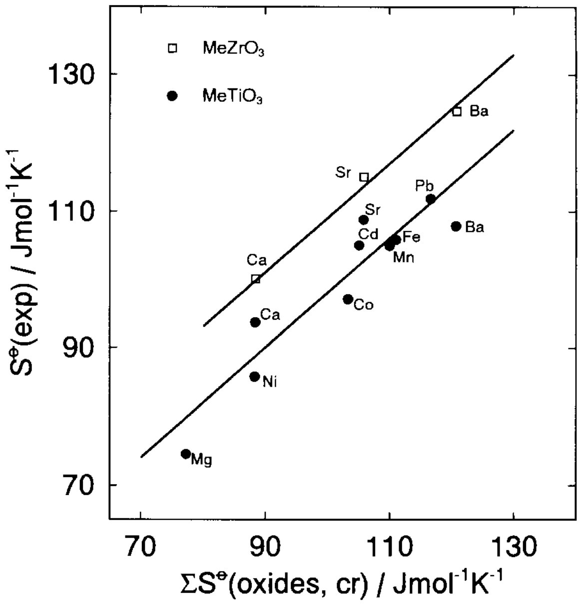

Fig. 3. Relationship between the experimental entropies for titanates and zirconates and their constituent oxides.

the relationship between the quantities $(S^\ominus - V^\ominus)$ for zirconates or titanates and corresponding oxides are straight lines as illustrated in Fig. 4. These lines are represented by the equations

$$(S^\ominus - V^\ominus)(\text{MeZ, cr}) = 0.780 \sum n_i (S_i^\ominus - V_i^\ominus) + 23.3 \quad \text{for zirconates} \qquad (16a)$$

$$(S^\ominus - V^\ominus)(\text{MeZ, cr}) = 0.990 \sum n_i (S_i^\ominus - V_i^\ominus) - 2.57 \quad \text{for titanates} \qquad (16b)$$

The relative average absolute deviations for zirconates and titanates are 0.0061 and 0.0336, respectively. The relationship (16a) can be used to estimate the entropy of $PbZrO_2$ at

$$S^\ominus(\text{PbZrO}_3, \text{cr}) = 124.5 \text{ J mol}^{-1} \text{ K}^{-1} \qquad (17)$$

The entropy estimates from different methods, i.e., 125.9 J mol^{-1} K^{-1} from Eq. (12), 124.2 J mol^{-1} K^{-1} from Eq. (13a), and 124.5 J mol^{-1} K^{-1} from Eq. (16a) are in very close agreement. In addition, it is worthwhile to compare the entropy of formation of $PbZrO_3$ from oxides calculated from Eqs. (3) and (10) with those estimated using the proposed methods. Our estimates from Eqs. (12), (14) and (17) are 6.8, 5.1 and 5.4 mol^{-1} K^{-1}, respectively. They agree with the value of 7.47 obtained from Eq. (3), but disagree with the value of 21.43 obtained from Eq. (10). In general, a method for predicting entropies can be chosen on the basis of the availability of input parameters.

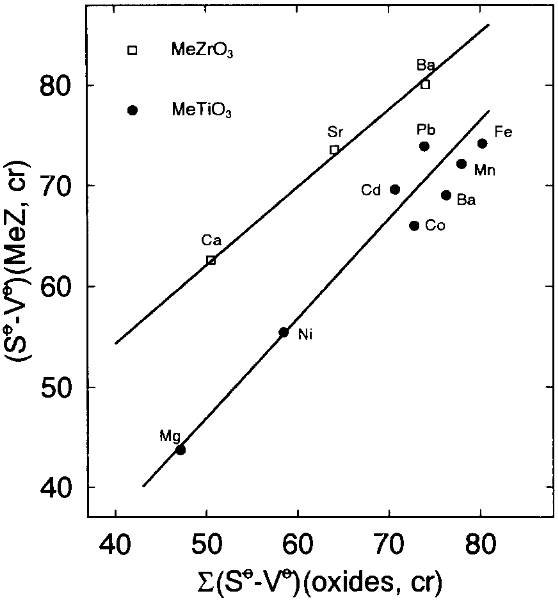

Fig. 4. Correlation between the differences between experimental entropies and molar volumes for titanates and zirconates and their constituent oxides.

4. Heat capacity

Historically, heat capacity $C_p^{\ominus}$ was the first property for which estimation techniques were developed [30,31]. Most modern methods based on atomic or group contributions give an accuracy of 6–12% [6,32]. A reasonably accurate method (approx. 6%) was proposed by Kubaschewski and Ünal [33]. However, their method requires the melting point for the estimation of the temperature dependence of $C_p^{\ominus}$, which makes the method difficult to use for many compounds. Therefore, we propose to estimate the heat capacity of compounds of the type $Me^{II}Me^{IV}O_3$ as a sum of heat capacities for $Me^{II}O$ and $Me^{IV}O_2$

$$C_p^{\ominus}(Me^{II}Me^{IV}O_3, \text{cr}, T) = C_p^{\ominus}(Me^{II}O, \text{cr}, T) + C_p^{\ominus}(Me^{IV}O, \text{cr}, T) \quad (18)$$

This method is based on the assumption that the heat capacity change for the formation of $Me^{II}Me^{IV}O_3$ from oxides is equal to zero, which is frequently used in practical calculations [6,29]. Fig. 5 illustrates the deviations between heat capacities predicted using this procedure and experimental data for metal zirconates and titanates. As shown in Fig. 5, the deviations are usually between 0 and 3% and uniformly scattered around zero. Therefore, we may apply this technique with confidence to $PbZrO_3$. The predicted heat capacity is

$$C_p^{\ominus}(PbZrO_3, \text{cr}) = 114.700 + 20.536 \times 10^{-3}T - 16.8780 \times 10^{5}T^{-2} \quad (\text{J mol}^{-1}\ \text{K}^{-1}) \quad (19)$$

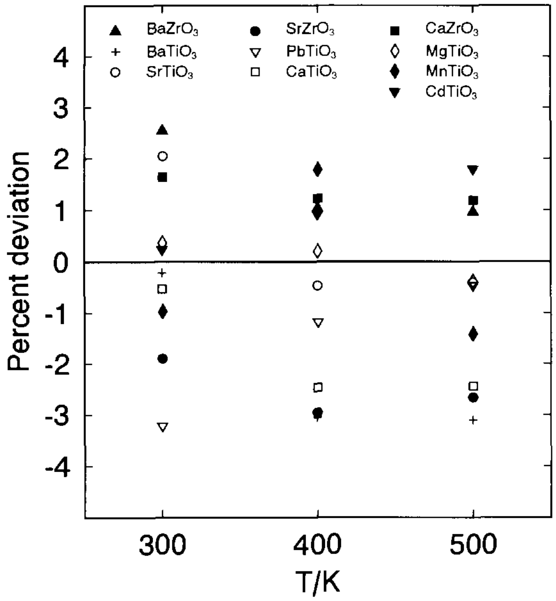

Fig. 5. Deviations between experimental heat capacities for various metal zirconates and titanates and those calculated from the data for constituent oxides.

5. Conclusions

It has been demonstrated that the standard-state thermochemical properties of perovskite-type crystalline solids obey well-defined linear correlations within families of compounds (such as titanates and zirconates). In some cases, e.g., for the prediction of heat capacities, these methods are generalized to any compound, not necessarily belonging to a certain family. These correlations can be utilized to predict the thermochemical properties of compounds that have not been experimentally investigated. Such estimations have been made for lead zirconate ($PbZrO_3$), which is an important material for ceramic applications.

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