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Thermodynamic Properties and Stability of In-Doped $SrCeO_3$ Proton-Conducting Ceramics

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The standard enthalpy of formation of $SrCe_{0.5}In_{0.5}O_{2.75}$ has been determined by solution calorimetry by combining the solution enthalpies of $SrCe_{0.5}In_{0.5}O_{2.75}$ and a $SrCl_2$ + $0.5CeCl_3$ + $0.5InCl_3$ mixture in 1.0 M HCl with KI as a solvent at 298.15 K and literature data. The results show that $SrCe_{0.5}In_{0.5}O_{3-\delta}$ is thermodynamically stable with respect to decomposition to binary oxides. Calculation of the Gibbs energies for the interaction of $SrCe_{0.5}In_{0.5}O_{2.75}$ with aluminum oxide and zirconium dioxide allows one to predict that $SrCe_{0.5}In_{0.5}O_{2.75}$ does not react with Al_2O_3 or ZrO_2 at ambient temperatures.

Introduction

Studies of high-temperature proton conductors (HTPC) have intensified in the last ten years,[1–12] because these materials have wide enough technological application as materials in fuel cells, sensors, electrocatalysis, hydrogen separation membranes, and so on. Conversion of hydrogen using a solid oxide fuel cell with a proton-conducting electrolyte occurs at an intermediate temperature (700–1100 K) without expensive electrocatalysts or the necessity to recirculate the fuel. The advancement of hydrogen separation technology has become important in energy applications for the production of petrochemicals and pure hydrogen, the latter being of particular interest for use in fuel cells. Accordingly, high-temperature proton-conducting oxides have received increasing attention for these applications. The most well-known HTPC materials are the perovskite oxides (ABO_3) with large basic A cations (e.g., Ba, Sr) and tetravalent B cations (e.g., Zr, Ce). A lot of research has been devoted to the study of ionic conductivity. However, for practical applications, the study of other properties is required. For example, one of the important properties is stability and, in particular, thermodynamic stability. As has been already found, the thermodynamic stability can have an influence on the mechanical stability of the microstructure. However, there has not been enough research devoted to studying of thermodynamic stability of doped cerates. Furthermore, the thermodynamic properties connected with structural parameters can be used to understand the correlation of structure and stability in solid solutions $A(II)Ce_{1-x}B(III)_xO_{3-\delta}$ [A(II) – metal of the second group, B(III) – metal of the third group].

This work forms part of the investigations performed by authors on barium and strontium cerates and is devoted to a thermodynamic study of $SrIn_{0.5}Ce_{0.5}O_{3-d}$. In an earlier paper,[5–6] we reported studies on barium cerates doped with rare-earth elements. However, as we reported, the dopant solubility limit is less than 20% of the available B sites (ABO_3 structure), and therefore, the possibility of introducing protonic defects into the matrix is also limited. Consequently, it is interesting to study other dopants of the B sites of ABO_3 with the aim of investigating the possibility of increasing the dopant limits and to find ionic conductors with ionic conductivities that change over wide limits. For this reason, we decided to investigate the compounds $SrIn_{0.5}Ce_{0.5}O_{3-d}$ and their thermodynamic stability towards both binary oxides and external reagents such as Al_2O_3 and ZrO_2.

Results and Discussion

To determine the thermodynamic data for the $SrCe_{0.5}In_{0.5}O_{3-d}$ we used the thermochemical cycle, which is similar to one applied in ref.[6] for barium cerates doped with rare-earth elements. The principal scheme is based on the dissolution of strontium cerate doped with indium as well as mixtures of strontium, cerium, and indium chlorides ($SrCl_2$ + $0.5CeCl_3$ + $0.5InCl_3$) in hydrochloric acid [HCl (sol)] with KI. The KI was added to convert Ce^{4+} to Ce^{3+}. In order to realize this cycle, we needed the following samples for the investigation: $SrCe_{0.5}In_{0.5}O_{3-d}$, $SrCl_2$, $CeCl_3$, and $InCl_3$.

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Previously, we used the expensive technique from the Karlsruhe Research Center that enables one to prepare different complex oxides of high quality.[2,6]

The phase purity and identity of $SrCe_{0.5}In_{0.5}O_{2.75}$ were confirmed by X-ray powder diffraction. We also performed analysis of samples with a sequential X-ray fluorescence spectrometer.

The sample $SrCe_{0.5}In_{0.5}O_{2.75}$ was shown to have a cubic structure (space group $Pm\bar{3}m$).[13] All compounds were also characterized by chemical analysis,[14–15] and analytical results are presented in Table 1. Analyses indicated that impurities of Ho, Dy, Yb, La, Tm, Er, Pr, Sm, Te, Ca, Mg, Mn, Pb, and Ag were present at levels of between 10^{-3} and 10^{-4} at.-%. The oxygen contents were determined by iodometric titration with 0.01 м $Na_2S_2O_3{\cdot}5H_2O$ according to the method described in ref.[16] According to the results of the chemical analysis, the sample had the composition $SrCe_{0.5}In_{0.5}O_{2.75}$.

Table 1. Analytical results.

Compound	Found (%)	Calculated (%)
$CeCl_3$	Ce, 56.81 ± 0.04	Ce, 56.85
$InCl_3$	In, 51.94 ± 0.03	In, 51.91
$SrCl_2$	Sr, 55.23 ± 0.04	Sr, 55.27
$SrCe_{0.5}In_{0.5}O_{2.75}$	Sr, 33.80 ± 0.04	Sr, 33.82
	In, 22.19 ± 0.03	In, 22.16
	Ce, 27.01 ± 0.03	Ce, 27.04
	O, 16.99 ± 0.02	O, 16.98

All calorimetric experiments were performed in an automatic calorimeter with an isothermal jacket. The calorimeter consists of a Dewar vessel with a brass cover (V = 200 mL). The platinum resistance thermometer, calibration heater, cooler, mixer, and the device to break the ampoules were mounted on the lid of the Dewar vessel. Detailed descriptions of the construction and the procedures for performing experiments and checking the calorimeter are presented in refs.[6,14–15] The computer controller for the platinum thermometer and the Matlab program were written at our laboratory. The program allows one to measure and record the temperature of the vessel, calibrate the instrument with precise injections of electrical energy and calculate calorimeter constants and enthalpies. The calorimetric vessel was maintained at 298.15 K with a temperature drift of less than 0.0003 K over 10 h. Dissolution of potassium chloride in water was performed to check the precision of the calorimeter. The obtained dissolution heat of KCl was 17.41 ± 0.04 $kJ\,mol^{-1}$ (the molality of the final solution was 0.028 $mol\,kg^{-1}$). The certified values are 17.42 ± 0.02 $kJ\,mol^{-1}$ in ref.[17] and 17.47 ± 0.07 $kJ\,mol^{-1}$ in ref.[18]

A solution of 1 м HCl with 0.1 м KI was chosen as a solvent. A mixture of $SrCl_2$, $CeCl_3$, and $InCl_3$ was prepared in a ratio of 1:0.5:0.5. This solvent was also used by the authors[19] to determine the enthalpies of formation of $BaCeO_3(s)$ and $SrCeO_3(s)$. The reactions showing the thermochemical cycle from which the standard enthalpy of formation of $SrCe_{0.5}In_{0.5}O_{2.75}$ was calculated are presented in Table 2.

The molar concentration of $CeCl_3$ in our experiments was the same as that in ref.[19] We used some data from this paper for our calculation, for example, the enthalpies of solution of KI and I_2, which were reported with high precision.[19] We measured only dissolution enthalpies of $SrCe_{0.5}In_{0.5}O_{2.75}$ and the mixture $SrCl_2$ + $0.5CeCl_3$ + $0.5InCl_3$. The cycle was completed with the auxiliary values for the molar enthalpies of formation of H_2O(aq.), HCl(aq.), $SrCl_2(s)$, $CeCl_3(s)$, $InCl_3(s)$, KCl(s), and KI(s).

All manipulations with $CeCl_3$, $SrCl_2$, and $InCl_3$ were performed in a dry box (pure Ar gas) to prevent interaction with moisture or CO_2. The mass of $SrCe_{0.5}In_{0.5}O_{2.75}$ used for the experiments was about 0.1 g.

The measured enthalpies of solution of $SrCe_{0.5}In_{0.5}O_{2.75}$ and ($SrCl_2$ + $0.5CeCl_3$ + $0.5InCl_3$) were determined as $\Delta_{sol}H^0{}_1(298.15\ K) = -216.5 \pm 2.8\ kJ\,mol^{-1}$ (n = 6) and $\Delta_{sol}H^0{}_2(298.15\ K) = -158.87 \pm 0.68\ kJ\,mol^{-1}$ (n = 6) (n = number of parallel calorimetric experiments). Errors were calculated for the 95% confidence interval by using standard procedures for treatment of experimental results.[20]

Table 2. Thermochemical cycle for the determination of the enthalpy of formation of $SrCe_{0.5}In_{0.5}O_{2.75}$.[a]

Reactions		$\Delta_{sol}H^{o}{}_m$ (kJ)	Ref.
$SrCe_{0.5}In_{0.5}O_{2.75}(s) + (5.5HCl + 0.5KI)(sol) \rightarrow (SrCl_2 + 0.5CeCl_3 + 0.5InCl_3 + 0.5KCl + 0.25I_2 + 2.75H_2O)(sol)$	(1)	−216.5 ± 2.8	This work
$SrCl_2(s) + 0.5CeCl_3(s) + 0.5InCl_3(s)$ + (solution 1) $\rightarrow (SrCl_2 + 0.5CeCl_3 + 0.5InCl_3)(sol)$	(2)	−158.87 ± 0.68	This work
$2.75H_2(g) + 1.375O_2(g)$ + (solution 1) $\rightarrow 2.75H_2O(sol)$	(3)	−786.06 ± 0.12	[19]
$0.5KI(s)$ + (solution 1) $\rightarrow 0.5KI(sol)$	(4)	+10.42 ± 0.18	[19]
$0.5K(s) + 0.25I_2(s) \rightarrow 0.5KI(s)$	(5)	−164.58 ± 0.07	[19]
$0.25I_2(s)$ + (solution 1) $\rightarrow 0.25I_2(sol)$	(6)	+1.39 ± 0.25	[19]
$0.5KCl(s)$ + (solution 1) $\rightarrow 0.5KCl(sol)$	(7)	+9.00 ± 0.03	[19]
$0.5K(s) + 0.25Cl_2(g) \rightarrow 0.5KCl(s)$	(8)	−218.23 ± 0.06	[19]
$2.75H_2(g) + 2.75Cl_2(g)$ + (solution 1) $\rightarrow 5.5HCl(sol)$	(9)	−903.98 ± 0.06	[19]
$Sr(s) + Cl_2(g) \rightarrow SrCl_2(s)$	(10)	−832.43 ± 0.85	[19]
$0.5Ce(s) + 0.75Cl_2(g) \rightarrow 0.5CeCl_3(s)$	(11)	−530.27 ± 0.26	[19]
$0.5\,In(s) + 0.75Cl_2(g) \rightarrow 0.5InCl_3(s)$	(12)	−268.6 ± 2.2	[17]
$Sr(s) + 0.5In(s) + 0.5Ce(s) + 1.375O_2(g) \rightarrow SrCe_{0.5}In_{0.5}O_{2.75}(s)$	(13)	−1509.4 ± 3.4	This work

[a] In the table, "solution 1" refers to a 1 м solution of HCl in 0.1 м KI.

The enthalpies of dissolution measured for reactions 1 and 2 and data on reactions 3–12 (see Table 2) were used for calculating the enthalpy of the reaction Sr(s) + 0.5Ce(s) + 0.5In(s) + $1.375O_2$(g) → $SrCe_{0.5}In_{0.5}O_{2.75}$(s) + $\Delta_rH_{13}^o$ as follows: $\Delta_fH_{13}^o = -\Delta_{sol}H_1^o + \Delta_{sol}H_2^o + \Delta_{sol}H_3^o - \Delta_{sol}H_4^o - \Delta_{sol}H_5^o + \Delta_{sol}H_6^o + \Delta_{sol}H_7^o + \Delta_{sol}H_8^o - \Delta_{sol}H_9^o + \Delta_{sol}H_{10}^o + \Delta_{sol}H_{11}^o + \Delta_{sol}H_{12}^o$.

Here, $\Delta_fH_{13}^o = \Delta_fH^o(SrCe_{0.5}In_{0.5}O_{3-\delta}$, s, 298.15 K) = –1509.4 ± 3.4 kJ mol^{-1} is the standard enthalpy of formation of strontium cerate doped with indium oxide.

To calculate this value, we used our experimental results and literature data for the enthalpies of formation of different compounds and processes taken from refs.[17,19] and presented in Table 2.

Experimental data have also been used to study the thermodynamic stabilities of the investigated compounds with the respect to mixtures of the same nominal composition. Enthalpies of formation of SrO, CeO_2, and In_2O_3 taken from the literature[17] were used to calculate the enthalpies of formation of $SrCe_{0.5}In_{0.5}O_{2.75}$ from binary oxides as follows:

$$SrO(s) + 0.5CeO_2(s) + 0.25In_2O_3(s) \rightarrow SrCe_{0.5}In_{0.5}O_{2.75}(s) \quad (14)$$

$$\Delta_{ox}H^0\ (298.15\ K) = -142.5 \pm 4.3\ kJ\ mol^{-1}$$

In order to understand whether $SrCe_{0.5}In_{0.5}O_{2.75}$ is stable or unstable with respect to decomposition to a SrO(s) + $0.5CeO_2$(s) + $0.25In_2O_3$(s) mixture, it is necessary to know the Gibbs energy ($\Delta G = \Delta H - T\Delta S$) of reaction 14. There is no entropy value for the $SrCe_{0.5}In_{0.5}O_{2.75}$ phase in the literature. This value was estimated by using entropies of CeO_2, In_2O_3, and $SrCeO_3$ taken from refs.[17,19] The method of estimation of the entropies of complex oxides as a sum of the binary or triple oxides is frequently used and gives good results. For example, the entropies of the $YBa_2Cu_3O_{6.5}$ phase estimated as the sum of the entropies of $2BaCuO_2$, CuO, and $0.5Y_2O_3$ is 321.8 J(K mol)$^{-1}$, whereas the measured entropy is 321.7 J(K mol)$^{-1}$.

The Gibbs energy for process 14 was estimated as $\Delta_{ox}G^0$ (298.15 K) = –146.6 ± 4.3 kJ mol^{-1} by using the formation enthalpy of reaction 14, the entropies of SrO, CeO_2, In_2O_3, as well as the estimated entropy of $SrCe_{0.5}In_{0.5}O_{2.75}$.

As can be seen, strontium cerate doped with indium is thermodynamically stable with respect to its decomposition into binary oxides at room temperature. This is not an obvious result for this class of compounds, because there is a discussion about the thermodynamic stability of $SrCeO_3$.[19,21,22] Here it is necessary to note the following: it was proved and reported in a paper[23] that a single-phase material in $Sr_{1+x}CeO_{3+\delta}$ solid solutions was obtained for compositions x = 0.02–0.03. Therefore, it is possible to assume that authors[19,21,22] who obtained different data on the formation enthalpies and thermodynamic stability of strontium cerate performed measurements for different compositions. It is not possible to clear the discrepancy, because the full chemical analysis of $SrCeO_3$ is not presented in the literature.[19,21,22]

It is interesting to mention that the enthalpy of formation of complex oxides from binary oxides is usually close to zero [for example, $\Delta_{ox}H$(298.15 K, $CdSiO_3$) = –6.28 kJ mol^{-1}]. In our case, we have values around –150 kJ mol^{-1}, which is higher than the usual values for complex oxides. Hence, this compound is thermodynamically stable enough.

As some researchers have pointed out, a concern for barium or strontium cerates is their stability in the external atmosphere. When pellets of $SrCeO_3$ were sintered in an alumina or zirconia container, it is possible to assume that $SrCeO_3$ can react with Al_2O_3 or ZrO_2 and decompose through the following reactions: $SrCeO_3 + Al_2O_3 \rightarrow SrAl_2O_4 + CeO_2$ and $SrCeO_3 + ZrO_2 \rightarrow SrZrO_3 + CeO_2$.

In relation to this, it was interesting to understand whether $SrCe_{0.5}In_{0.5}O_{2.75}$ reacted with Al_2O_3(s) or ZrO_2(s). For this reason we considered the following reactions:

$$SrCe_{0.5}In_{0.5}O_{2.75}(s) + Al_2O_3(s) \rightarrow SrAl_2O_4 + 0.5CeO_2(s) + 0.25In_2O_3(s) \quad (15)$$

$$SrCe_{0.5}In_{0.5}O_{2.75}(s) + ZrO_2(s) \rightarrow SrZrO_3 + 0.5CeO_2(s) + 0.25In_2O_3(s) \quad (16)$$

The possibility of interaction was estimated by using our experimental data, formation enthalpies, and entropies of the phases CeO_2, In_2O_3, $SrAl_2O_4$, $SrZrO_3$ taken from ref.[17]

It is necessary to note that the direction of any chemical transformation is determined by the sign of the Gibbs energy $\Delta G^o = \Delta H^o - T\Delta S^o$. Below we show the calculated Gibbs energies for reactions 15 and 16. As was mentioned earlier, the value of the entropy of $SrCe_{0.5}In_{0.5}O_{2.75}$, which is absent in the literature, was estimated by using the entropies of In_2O_3, $SrCeO_3$, and CeO_2 taken from refs.[17,19] The Gibbs energies for processes 15 and 16 were calculated as Δ_rG^o (298.15 K) = +85.7 ± 8.1 kJ mol^{-1} and Δ_rG^o (298.15 K) = +69.4 ± 6.4 kJ mol^{-1}, respectively.

Taking into account the Gibbs energies of reactions 15 and 16, it is possible to predict that $SrCe_{0.5}In_{0.5}O_{2.75}$ does not react with Al_2O_3 and ZrO_2 at ambient temperatures. This behavior was not expected, since according to ref.[6], complex oxides $BaCe_{0.8}Nd_{0.2}O_{2.9}$ and $BaCe_{0.8}Lu_{0.2}O_{2.9}$ react with Al_2O_3 and ZrO_2 at ambient temperatures. The presented results indicate that the compound $SrCe_{0.5}In_{0.5}O_{2.75}$ is a prospective material for application in fuel cells, sensors, electrocatalysis, hydrogen separation membranes, and so on.

Conclusions

In this paper we report values for the standard formation enthalpies of $SrCe_{0.5}In_{0.5}O_{2.75}$ measured by solution calorimetry in a solution of 1 M HCl in 0.1 M KI. We determined the thermodynamic stability of In-doped strontium cerate with respect to mixtures of binary oxides, the enthalpies, and Gibbs energies of interaction with alumina and zirconia. On the basis of these data, we established that the above-mentioned oxide is thermodynamically stable with respect to decomposition into binary oxides at room temperature. It is also possible to predict that $SrCe_{0.5}In_{0.5}O_{2.75}$ does not react with Al_2O_3 and ZrO_2 at room temperature.

Experimental Section

The phase of composition $SrCe_{0.5}In_{0.5}O_{3-d}$ was prepared by solid-state synthesis from $SrCO_3$, In_2O_3, and CeO_2. Synthesis was performed according to the reaction: $SrCO_3 + 0.5CeO_2 + 0.25In_2O_3 \rightarrow CO_2 + SrCe_{0.5}In_{0.5}O_{2.75}$. The reagents $SrCO_3$ (99.999%, CERAC, TM incorporated), CeO_2 (99.99%, Vetron GmbH), and In_2O_3 (99.99%, Reacton, A Johnson Matthey Company) were used for synthesis of the complex oxides $SrCe_{0.5}In_{0.5}O_{3-d}$. Stoichiometric amounts of $SrCO_3$, CeO_2, and In_2O_3 were mixed by ball milling in an agate container with agate balls using a planetary mill (FRITSCH pulverisette) over 72 h. The ground materials were palletized by using a 10 mm diameter die and fired at 1300 K for 70 h, at 1400 K for 10 h, or at 1700 K for 24 h using a CARBOLITE furnace. Detailed procedures of the preparation of analogous compounds were described in our earlier papers.[2,6]

Anhydrous $SrCl_2$ was prepared by drying $SrCl_2$ (CERAC, TM incorporated, USA, 99.9%) in argon at about 500 K. $CeCl_3$ was also purchased from CERAC (mass fraction is more then 0.999) and purified by vacuum sublimation in order to remove the lanthanide oxychloride impurities. For this purpose, $CeCl_3$ was sublimed above the melting temperature (1143 K) in a vacuum better than 10^{-5} Pa. $InCl_3$ was synthesized from Cl_2 and In. Chlorine gas was passed over indium at a temperature of about 450 K. All manipulations with $CeCl_3$, $BaCl_2$, and $InCl_3$ were performed in a dry box (pure Ar gas).

X-ray powder diffraction was performed with a STADI-P Stoe diffractometer (Germany, Cu-$K_{\alpha 1}$ radiation). An ARL ADVANT′XP sequential X-ray fluorescence spectrometer was also used to analyze the samples.

For the analysis of In and Ce, a spectrophotometric method (spectrophotometer SF–46) was used. Sr was determined by flame photometry (air/acetylene, Hitachi Z-8000). The content of impurities was determined by spectroscopic methods (mass spectrometer "Element", Finnigan Mat, Germany).

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[1] N. Fernandez, M. F. Garcia, *Eur. J. Inorg. Chem.* **2003**, *13*, 2458–2462.
[2] Th. Zeiske, R. Sonntag, D. Hohlwein, N. H. Andersen, Th. Wolf, *Nature* **1991**, *353*, 542–544.
[3] A. I. Ruiz, M. L. Lopez, M. L. Veiga, C. Pico, *Eur. J. Inorg. Chem.* **2000**, *4*, 659–664.
[4] T. Norby, M. Wideroe, R. Glockner, Y. Larring, *Dalton Trans.* **2004**, *19*, 3012–3018.
[5] B. C. H. Steele, A. Heinzel, *Nature* **2001**, *414*, 345–352.
[6] N. I. Matskevich, Th. Wolf, M. Yu. Matskevich, T. I. Chupakhina, *Eur. J. Inorg. Chem.* **2009**, *11*, 1477–1482.
[7] G. C. Mather, M. S. Islam, *J. Mater. Chem.* **2005**, *17*, 1736–1744.
[8] A. Selmi, G. Corbel, S. Kojikian, V. Voronkova, E. Kharitonova, P. Lacorre, *Eur. J. Inorg. Chem.* **2008**, *11*, 1813–1821.
[9] K. D. Kreuer, S. J. Paddison, E. Spohr, M. Schusher, *Chem. Rev.* **2004**, *104*, 4637–4678.
[10] X. Weng, P. Boldrin, I. Abrahams, S. J. Skinner, J. A. Darr, *Chem. Mater.* **2007**, *19*, 4382–4384.
[11] Z. Shao, S. M. Haile, *Nature* **2004**, *43*, 170–173.
[12] G. C. Mather, F. M. Figueiredo, J. R. Paz, S. Garcia-Martin, *Inorg. Chem.* **2008**, *47*, 921–929.
[13] Th. Wolf, N. I. Matskevich, C. Greaves, *First Russian-German Seminar "Thermodynamics and Materials Science" Proceedings*, **2008**, 23–25 September, Novosibirsk, Russia, pp. 101–102.
[14] N. I. Matskevich, Th. Wolf, Yu. I. Pochivalov, *Inorg. Chem.* **2008**, *47*, 2581–2584.
[15] N. I. Matskevich, C. Greaves, *Thermochim. Acta* **2007**, *459*, 125–126.
[16] A. I. Nazzal, V. Y. Lee, E. M. Engler, R. D. Jacowitz, Y. Tokura, J. B. Torrance, *Phys. C* **1988**, *153–155*, 1367–1368.
[17] V. P. Glushko, *Termicheskie Konstanty Veshchestv (Thermal Constants of Substances)*, VINITI, Moscow, **1965–1982**, issues *1–10*.
[18] C. Gunter, R. Pfestorf, M. Rother, J. Seidel, R. Zimmermann, G. Wolf, V. Schroder, *J. Therm. Anal. Calorim.* **1988**, *33*, 359–363.
[19] E. H. P. Cordfunke, A. S. Booij, M. E. Huntelaar, *J. Chem. Thermodyn.* **1998**, *30*, 437–447.
[20] B. N. Oleinik, *Precision Calorimetry*, Publishing House of Standards, Moscow. **1973**, p. 207.
[21] C. W. Tanner, A. V. Virkar, *J. Electrochem. Soc.* **1996**, *143*, 1386–1389.
[22] J. Goudiakas, R. G. Haire, J. Fuger, *J. Chem. Thermodyn.* **1990**, *22*, 577–587.
[23] G. C. Mather, F. M. Figuiredo, J. R. Paz, S. G. Martin, *Inorg. Chem.* **2008**, *47*, 921–929.

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