Experimentation and thermodynamic modelling on SrZrO₃

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Abstract: Experimental data for the perovskite phase SrZrO₃ were subjected to a critical thermodynamic assessment using the CALPHAD approach. Special attention was paid to the structural behavior of SrZrO₃ to illustrate, how to select an appropriate thermodynamic model based on crystal structure and chemistry information, how to identify and resolve the inconsistency between various kinds of experimental data, and how to use thermodynamic modeling as a basic tool in the development and optimization of materials and process. Our assessment results in a Gibbs energy function covering the temperature range between 300 K and the melting point, which explains the experimental data within the experimental uncertainty.

Key words: thermodynamic modelling; CALPHAD; SrZrO₃; experimentation; interaction

1 Introduction

SrZrO₃ has been the subject of several investigations because of its technological applications. For instance, SrZrO₃ can be used in the electronic industry as insulators, and its refractory properties are of interest in high-temperature applications. In nuclear safety studies, SrZrO₃ plays an important role as it is formed in the UO₂ fuel by reaction between the fission products in the fuel matrix, and during core-concrete interactions between the fission products and the oxidized zircaloy cladding. The thermodynamic properties, the structural variants and phase transitions are thus of special interest as they influence the behaviour of hazardous fission products.

While due to the slight distortion, impurities, minor departures from nominal stoichiometry, or changes in synthesis temperatures, great discrepancy existed among the reported experimental data. In this way, thermodynamic modeling on SrZrO₃ was carried out in the present study, aiming to validate experimental results from literature and to provide a set of consistent thermodynamic parameters.

2 Evaluation of experimental data in literature

2.1 Structural information

There is continuous interest in the structural variants and phase transitions in SrZrO₃, associated with the technological application. However, because of the slight distortion, it has been argued that impurities, minor departures from nominal stoichiometry, or changes in synthesis temperatures could result in different crystal symmetries and phase transformations of SrZrO₃, thus two different reviews about the crystallographic structure of SrZrO₃ existed in Refs.[1−12]. One was that the room temperature structure of SrZrO₃ was pseudo-cubic[1−4], and this pseudo-cubic structure did not undergo any phase transformation upon heating[2−3]. The second review was that the room temperature structure of SrZrO₃ was orthorhombic[5−12], and the orthorhombic perovskite SrZrO₃ (o-SrZrO₃), in *Pnma*, will transform through higher symmetries during heating, eventually to ideal cubic (c-SrZrO₃)[9−13]. Very early, MEGAW[1], SMITH and WELCH[2] indexed the room temperature structure of SrZrO₃ to pseudo-cubic. MATHEWS et al[3]

failed to detect any phase transformation of pseudo-cubic $SrZrO_3$ in the temperature range between 298 and 1 675 K by high-temperature XRD, ROOSMALEN et al[4] owned the transformations of the pseudo-cubic samples to the impurities and lattice defects governed by the preparation temperature. On the other hand, very good start work on the structural transformations of $SrZrO_3$ was carried out by CARLSOON[8], who adopted XRD and differential thermal analysis(DTA) methods. The observations of CARLSOON[8] as to the sequence of phases were summarized as: o-$SrZrO_3$ (orthorhombic)→ p-$SrZrO_3$ (pseudo-tetragonal)→t-$SrZrO_3$ (tetragonal)→ c-$SrZrO_3$ (cubic) at 1 000, 1 130 and (1 430±25) K. The occurrence of the structure transformations has been confirmed [9−11]. Very recently, KENNEDY and HOWARD[9] detected the sequent structure transformations by a high-resolution neutron powder diffraction method. YAMANAKA et al[10] and LIGNY and RICHET[11] suggested the transformation temperatures based on the specific heat anomalies in the c_p curve of $SrZrO_3$. These heat capacities were determined by differentiation of the least square fits of the experimental enthalpies. The very small enthalpies and entropies attached to the phase transformations were practically determined by LIGNY and RICHET[11] and JOCAB and WASEDA [12]. Because the experimental procedures were well controlled and the experimental results were generally consistent with each other[5−12], the second review about the structure of $SrZrO_3$ was accepted in this work.

2.2 Thermodynamic information

Several scholars[10−22] have investigated the thermodynamic properties of $SrZrO_3$. Using high-temperature differential calorimeter, NAGARAJAN et al[13] reported enthalpy increments (H_T−H_{298}) for $SrZrO_3$ from 1 030 to 1 687 K. Drop calorimetry was used by several investigators[14−16], for (H_T−H_{298}) measurements on $SrZrO_3$ from 300 K to 1 650 K, 526 K to 2 318 K, and 474.4 K to 906.3 K, respectively. CORDFUNKE and KONINGS[17] have also reported enthalpy values for $SrZrO_3$ in their compilations. GOSPODINOV and MARCHEV[18] reported enthalpy data for $SrZrO_3$ in the temperature range between 298 and 500 K by differential scanning calorimeter(DSC), and BANERJEE et al[19] determined (H_T−H_{298}) of $SrZrO_3$ by a precise high-temperature Calvet micro-calorimeter in the temperature range from 384.8 to 991 K. The crystallographic structure and purity of the samples used by these were not described very clearly, while in view of the preparation temperature, it seems most likely that their samples were orthorhombic. These

experimental data[13−16, 19] were in good agreement with each other and joined smoothly with the adiabatic measurements carried out by KING and WELLER[20]. Thus they were used to evaluate the Gibbs energy of orthorhombic $SrZrO_3$, o-$SrZrO_3$. Data from GOSPODINOV and MARCHEV[18] were too high to have any physical meaning and were excluded in this work. For the first time, LIGNY and RICHET[11] did systematic measurements on the enthalpy increment (H_T−H_{273}) and heat capacities of $SrZrO_3$, and their sample underwent the structure transformation from orthorhombic through tetragonal and eventually to ideal cubic in the temperature range from 300 to 1 800 K. The measured data by LIGNY and RICHET[11] were used to evaluate the Gibbs energy functions of o-$SrZrO_3$, p-$SrZrO_3$, t-$SrZrO_3$ and c-$SrZrO_3$.

The estimated thermodynamic properties of $SrZrO_3$ at 298.15 K, i.e. the enthalpy of formation $\Delta_f H_{298}$= (−1767.5±3) kJ/mol[12], heat capacity c_p(298 K)= (103.43±0.31) J/(mol·K)[20] and standard entropy S_{298}^{Θ} =(115.1±0.84) J/(mol·K)[20] were adopted so that the evaluation can be carried out practically, but a low weight factor was applied to them.

The Gibbs energy of formation of $SrZrO_3$ relative to the pure oxides in the temperature range from 960 to 1 210 K, and from 1 182 to 1 364 K have been determined by JOCAB and WASEDA[12] and LEVITSKII[21] using electromotive force, respectively. JOCAB and WASEDA[12] also reported the enthalpies of formation for $SrZrO_3$ from the component oxides in the temperature range from 960 to 1 210 K. The enthalpy values reported by JOCAB and WASEDA[12] were in good agreement with those reported by MUROMACHI and NAVROTSKY[22] at 1 060 K. These data were not used in the optimization. However, they were compared with the calculated results in order to check the final modelling.

3 Thermodynamic models

The Gibbs energy function $^{\Theta}G_i^{\Phi}(T) = G_i^{\Phi}(T) -H_i^{SER}$ for the component i (i = ZrO_2, SrO) in the phase Φ is expressed by Eqn.(1):

$$^{\Theta}G_i^{\Phi}(T) = a+bT+cT\ln T+dT^2+eT^{-1}+fT^3+gT^7+hT^{-9} \qquad (1)$$

where H_i^{SER} is the molar enthalpy of the component i at 298.15 K and 101 325 Pa in its standard element reference(SER) state, and T is the absolute temperature. The last two terms in Eqn.(1) are used only outside the ranges of stability[23], the term gT^7 is relative to the liquid below the melting point and hT^{-9} to the solid

phases above the melting point.

In the present work, the Gibbs energy functions of pure ZrO_2, ${}^{\Theta}G^l_{ZrO_2}$, ${}^{\Theta}G^c_{ZrO_2}$, ${}^{\Theta}G^t_{ZrO_2}$ and ${}^{\Theta}G^m_{ZrO_2}$ were taken from the assessments of DU et al[24]. The Gibbs energy functions of SrO, ${}^{\Theta}G^l_{SrO}$ and were taken from SGTE accepted substance database[25].

Since there were experimental thermodynamic data for o-SrZrO$_3$ in a wide temperature range[14−25], it was preferable to express the Gibbs energies relative to the SER state, and the following equation was used:

$$^{\Theta}G^o_{SrZrO_3} = a_1 + b_1 T + c_1 T\ln T + d_1 T^2 + e_1 T^{-1} \tag{8}$$

where the coefficients c_1, d_1 and e_1 can be evaluated based on the selected experimental enthalpy increments [14−19, 22] and heat capacities[11, 13, 15].

The Gibbs energies of p-SrZrO$_3$, t-SrZrO$_3$ and c-SrZrO$_3$ were evaluated based on those of o-SrZrO$_3$, neglecting any difference of heat capacity between these forms. The following equations were found sufficient to describe the solid-solid phase transformations of SrZrO$_3$ as well as the corresponding experimental data:

$$^{\Theta}G^p_{SrZrO_3} = {}^{\Theta}G^o_{SrZrO_3} + \Delta H_1 - T\cdot\Delta S_1 \tag{9}$$

$$^{\Theta}G^t_{SrZrO_3} = {}^{\Theta}G^p_{SrZrO_3} + \Delta H_2 - T\cdot\Delta S_2 \tag{10}$$

$$^{\Theta}G^c_{SrZrO_3} = {}^{\Theta}G^t_{SrZrO_3} + \Delta H_3 - T\cdot\Delta S_3 \tag{11}$$

where ΔH_i and ΔS_i (i=1, 2, 3) are the enthalpies and entropies of the transformations from o-SrZrO$_3$ to p-SrZrO$_3$, from p-SrZrO$_3$ to t-SrZrO$_3$, and from t-SrZrO$_3$ to c-SrZrO$_3$, respectively, which were evaluated by using the corresponding thermodynamic data[13−15].

4 Optimization procedure

The optimization was conducted using the Thermo-calc software package[26]. The critically selected experimental data were processed with a specific weight factor reflecting the experimental uncertainty. The optimization process consists of four steps.

In the first step the measured heat capacities and enthalpy increments were fitted[11, 13−16, 19]. In the next step the Gibbs energy functions of o-SrZrO$_3$ from room temperature up to about 1 023 K were constructed by using the enthalpy of formation and the entropy values at 298.15 K[12, 20]. In the third step the Gibbs energy function of o-SrZrO$_3$ for the derivation of the Gibbs energy of p-SrZrO$_3$, t-SrZrO$_3$, c-SrZrO$_3$ and the enthalpy and temperature of transformation in the analysis of thermodynamic properties[13−22] and structural behavior were obtained[4−12]. To achieve this,

the reported enthalpies and entropies of the transformations from o-SrZrO$_3$ to p-SrZrO$_3$ and from p-SrZrO$_3$ to t-SrZrO$_3$ were included[11−12]. By considering the solid-state transformation between the tetragonal and cubic structure, a small value of 1 J/(mol·K) was assumed for the corresponding entropy change. The Gibbs energy expressions obtained in this way are suitable for explaining the selected thermodynamic properties and structural information and making predictions of thermodynamic properties in multi-component systems. In the last step all model parameters were assessed simultaneously in a least squares optimization to represent the key experimental data within experimental uncertainty.

5 Results

The model parameters obtained from the optimization process are presented in Table 1. These parameters together with evaluated Gibbs energy functions for ZrO_2[24], and SGTE recommended Gibbs energies for SrO[25] allow the calculation of thermodynamic and structural properties of SrZrO$_3$. In Table 1 the calculated enthalpy and entropy of SrZrO$_3$ at 298.15 K are also presented. To enhance a comparison with experimental data, the enthalpy and entropy of transformations are calculated, the results of which are presented in Table 1, too. Figs.1 and 2 show calculated (H_T-H_{298}) and c_p of SrZrO$_3$, respectively. In order to check the final modeling parameters, the Gibbs energy and enthalpy of formation of SrZrO$_3$ relative to the pure oxides in some key temperatures are calculated and listed in Tables 2 and 3, respectively.
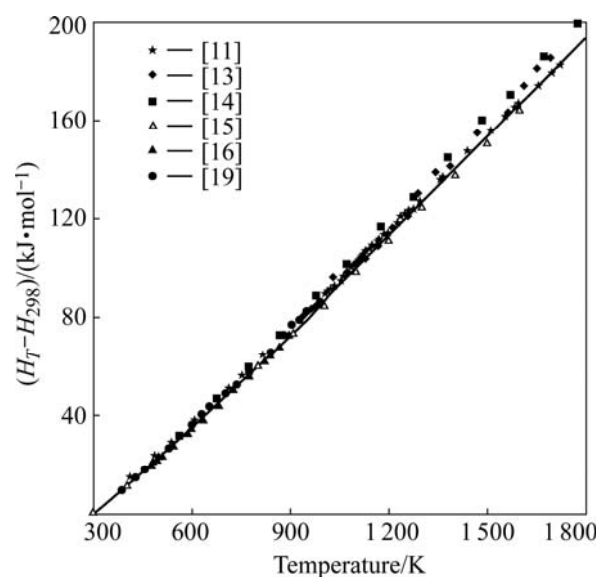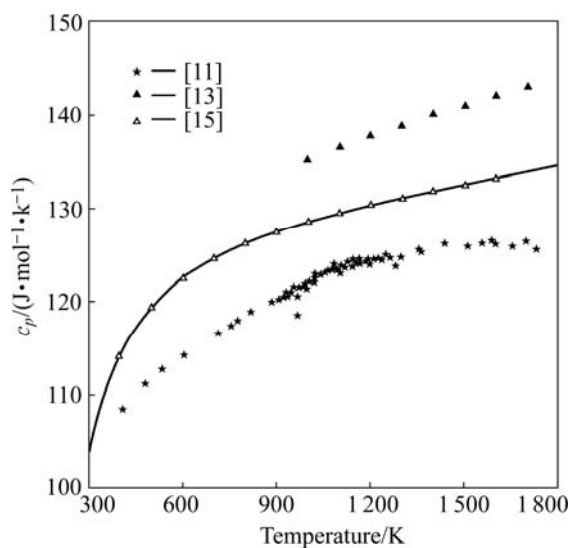

Fig.1 Calculated (H_T-H_{298}) of SrZrO$_3$ compared with measured data[11,13−16,19]

Table 1 Summary of thermodynamic properties of $SrZrO_3$ compound

Thermodynamic property at different temperatures	$10^{-3}\Delta H$	ΔS	c_p	Reference
298 K	$(-1\,767.5 \pm 3)$[15]	115.1 ± 0.84	103.43 ± 0.31	[20]
	$-1\,765$	115.1	103.4	This work
Transition temperature from orthorhombic to pseudo-tetragonal			$1\,000 \pm 25$	[8]
			$1\,023$	[9]
			$1\,041$	[10]
	1.5 ± 0.1	1.7 ± 0.3	995 ± 5	[11]
	1.521	1.51	$1\,007$	This work
Transition temperature from pseudo-tetragonal to tetragonal			$1\,130\pm25$	[8,10]
			$1\,113\pm10$	[9]
	0.5 ± 0.1	0.45 ± 0.3	$1\,105\pm5$	[11]
	1.123 ± 0.6	1.1 ± 0.5	$1\,123\pm10$	[12]
	0.686	0.612	$1\,121$	This work
Transition temperature from tetragonal to cubic			$1\,430\pm25$	[8,11]
			$1\,343\pm10$	[9]
			$1\,376\pm10$	[10]
	1.389	1	$1\,389$	This work

Gibbs energy of orthorhombic $SrZrO_3$: $^{\Theta}G_{SrZrO_3} = -1\,809\,275.23+733.058\,19T-124.659\,27T\ln 7-0.002\,923\,081\,5T^2+1\,026\,060.9T^{-1}$

Fig.2 Calculated heat capacity of $SrZrO_3$ compared with measured data[11, 13, 15].

Table 2 Comparison of Gibbs energies of formation of $SrZrO_3$ from component oxides

Temperature/K	$\Delta G(T)/(kJ\cdot mol^{-1})$		
	[12]	[21]	This work
1 000	-89.08 ± 3	-85.19 ± 4	-82.26
1 100	-90.50 ± 3	-85.55 ± 4	-83.36
1 200	-92.01 ± 3	-85.91 ± 4	-84.48
1 300	-93.54 ± 3	-86.27 ± 4	-85.56

6 Discussion

Fig.1 illustrates that our calculated (H_T-H_{298}) represents their measurements[11,13−16,19] within

Table 3 Comparison of enthalpy of formation of $SrZrO_3$ from component oxides

Temperature/K	$\Delta H(T)/(kJ\cdot mol^{-1})$		
	[12]	[22]	This work
298	-76.4 ± 2		-72.37
960−1 123	-74.9 ± 3		$-71.49\text{—}72.34$
1 060		-75.9 ± 4	-71.2

experimental uncertainty. Fig.2 indicates that our calculation on c_p of $SrZrO_3$ matches quite well with those of NAGARAJAN et al[13] and seems a compromise among the data of LIGNY and RICHET[11] and LEVITSKII et al[15]. Table 1 indicates that our calculated enthalpy and entropy values are consistent with available experimental data. In Tables 2 and 3, the thermodynamic quantities predicted by using the thermodynamic parameters are compared with two pieces of experimental information, which are not used in the modelling. Table 2 illustrates that the predicted Gibbs energy of formation of $SrZrO_3$ relative to the pure oxides reproduce the experimental values[12, 21] within the experimental errors. Table 3 illustrates that the predicted enthalpy of formation of $SrZrO_3$ relative to the pure oxides can reproduce the experimental values of Refs.[12, 22].

In order to check our calculated structural properties of $SrZrO_3$, the compound $SrZrO_3$ was prepared by solid reaction with the suitable ratio of $SrCO_3$ to ZrO_2 at 1 723 K. The obtained $SrZrO_3$ were heat-treated at 973 K, 1 123 K and 1 423 K, for 8 h, respectively, followed with air-quenching or furnace-cooling. The samples as-prepared were analysed with XRD to identify the phase

structure. As shown in Fig.3, the samples quenched from 1 423 K have cubic structure, and those furnace-cooled have orthorhombic structure, which confirms the polymorphic forms of SrZrO$_3$. While we failed to detect the tetragonal structure from the samples quenched from 1 123 K.
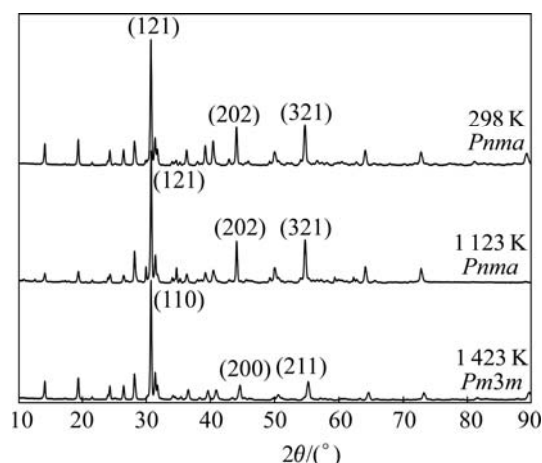

Fig.3 Observed XRD patterns from SrZrO$_3$, showing fundamental perovskite reflections

7 Conclusions

1) The phase transformation sequence of SrZrO$_3$ is estimated: orthorhombic → pseudo-tetragonal → tetragonal→cubic at 1 007 K, 1 121 K and 1 389 K, respectively. The relative enthalpies and entropies are 1.521 kJ/mol and 1.51 J/(mol·K), 0.686 kJ/mol and 0.612 J/(mol·K), 1.389 kJ/mol and 1 J/(mol·K) in sequence.

2) The thermodynamic function of orthorhombic SrZrO$_3$ is critically evaluated with all reliable experimental data reproduced within the estimated experimental uncertainty. The Gibbs energies of other three structures are estimated based on that of orthorhombic SrZrO$_3$.

References

[1] MEGAW H D. Crystal structure of double oxides of the perovskite type [J]. Proc Phys Soc, 1946, 58: 133−141.

[2] SMITH A J, WELCH A J E. Cation-size control of structure phase transitions in tin perovskites [J]. Acta Crystallogr, 1960, 13: 653−656.

[3] MATHEWS M D, MIRZA E B, MOMIN A C. High-temperature X-ray diffractometric studies of LaCrO$_3$ [J]. J Mater Sci Lett, 1991, 10: 3246−3248.

[4] VAN ROOSMALEN J A M, VAN VLAANDEREN, CORDFUNKE E H P. On the structure of SrZrO$_3$ [J]. J Solid State Chem, 1992, 101: 59−65.

[5] TILLOCA G, PEREZ M, JORBA Y. X-ray characterization of Sr$_3$Zr$_2$O$_7$ hydrate [J]. Res Intern Haut Temp Refract, 1964, 1: 331−342.

[6] AHTEE A, AHTEE M, GLAZER A M, HEWAT A W. The structural phase transitions in strontium zirconate revisited [J]. Acta Crystallogr B, 1976, 32: 3243−3246.

[7] KAMISHIMA O, HATTORI T, OHTA K, CHIBA Y, ISHIGAME M. Dielectric relaxation in Yb-doped SrZrO$_3$ [J]. J Phys: Condens Matter, 1999,11: 5355−5365.

[8] CARLSSON L. High-temperature phase transitions in SrZrO$_3$ [J]. Acta Crystallogr, 1967, 23: 901−905.

[9] KENNEDY B J, HOWARD C J. High-temperature phase transition in SrZrO$_3$ [J]. Phy Rev, 1999, 59(6): 4023−4027.

[10] YAMANAKA S, KUROSAKI K, OYAMA T, MUTA H, UNO M, MATSUDA T, KOBAYASHI S I. Thermodynamic properties of perovskite-type strontium cerate and zirconate [J]. J Am Ceram Soc, 2005, 88(6): 1496−1499.

[11] DE LIGNY D, RICHET P. High-temperature heat capacity and thermal expansion of SrTiO$_3$ and SrZrO$_3$ perovskite [J]. Phys Rev B, 1996, 53(6): 3013−3022.

[12] JACOB K T, WASEDA Y. Potentiometric determination of the Gibbs energies of formation of SrZrO$_3$ and BaZrO$_3$ [J]. Metall Mater Trans, 1995, 26B: 775−781.

[13] NAGARAJAN K, SAHA R, BABU R, MATHEWS C K. Thermodynamic functions of barium and strontium zirconates from calorimetric measurements [J]. Therm Acta, 1985, 90: 297−304.

[14] FOMICHEV E N, SLYNSAR N P, KRIVOROTENKO A D, TOLSTAYA V Y. Study of enthalpy of SrHfO$_3$ and SrZrO$_3$ at high temperature [J]. Ogneupory, 1973, 7: 36−37.

[15] LEVITSKII V A, TSAGAREISHVILI D S H, GVELESIANI G G. Enthalpy and specific heat of strontium and barium zirconates at high temperature [J]. High Temp, 1976, 14: 69−72.

[16] HUNTELAAR M E, CORDFUNKE E H P, VAN DER LAAN R R. Heat capacities and enthalpy increments of the metazirconates of calcium, strontium and barium [J]. Therm Acta, 1996, 274: 101−111.

[17] CORDFUNKE E H P, KONINGS R J M. Enthalpy increments of barium zirconate, BaZrO$_3$, and an assessment of its thermochemical properties [J]. Therm Acta, 1989, 156: 45−51.

[18] GOSPODINOV G G, MARCHEV V M. The temperature relations of the thermodynamic quantities of Ca, Sr, Ba, and Pb zirconates [J]. Therm Acta, 1993, 222: 137−141.

[19] BANERJEE A, DASH S, PRASAD R, SOOD D D. Enthalpy increments of strontium and barium zirconates [J]. Therm Acta, 1997, 298: 59−64.

[20] KING E G, WELLER W W. Thermochemistry and thermodynamic properties of substances (1) [M]. Washtington DC, US: US Bur Mines, 1960, 3.

[21] LEVITSKII V A. Thermodynamics of double oxides(I): Some aspects of the use of CaF$_2$-type electrolyte for thermodynamic study of compounds based on oxides of alkaline earth metals [J]. J Solid State Chem, 1978, 25: 9−22.

[22] MUROMACHI E T, NAVROTSKY A. Energetics of compounds (A^{2+}B^{4+}O$_3$) with the perovskite structure [J]. J Solid State Chem, 1988, 72: 244−256.

[23] ANDERSSON J O, GUILLERMET A F, GUSTAFSON P, HILLERT M, JANSSON B, SUNDMAN B, AGREN J. A new method of describing lattice stabilities [J]. Calphad, 1987, 11(1): 93−98.

[24] DU Y, JIN Z P, HUANG P Y. Thermodynamic calculation of the zirconia-calcia system [J]. J Am Ceram Soc, 1992, 75: 3040−3048.

[25] RISOLD D, HALLSTEDT B, GAUCKLER L J. The strontium-oxygen system [J]. Calphad, 1996, 20(3): 353−361.

[26] ANDERSON J O, HELANDER T, HOGLUND L, SHI P, SUNDMAN B. Thermo-Calc l & DICTRA, computational tools for materials science [J]. Calphad, 2002, 26(2): 273−312.

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