Available online at www.sciencedirect.com
SCIENCE DIRECT®
Thermochimica Acta 403 (2003) 267–273
thermochimica acta
www.elsevier.com/locate/tca

Specific heat capacity and Debye temperature of zirconia and its solid solution

C. Degueldre [a,*], P. Tissot [b], H. Lartigue [b], M. Pouchon [a]

[a] NES, Paul Scherrer Institut, 5232 Villigen-PSI, Switzerland
[b] CHIAM, Science II, University of Geneva, 1211 Geneva 4, Switzerland

Received 23 August 2002; received in revised form 19 December 2002; accepted 17 January 2003

Abstract

Specific heat C_P of zirconia and yttria stabilized zirconia doped or not with erbia and ceria was measured from 128 to 823 K and of yttria stabilized zirconia doped with erbia and plutonia from 443 to 1573 K. The new determined data were modelled using Debye theory. Data for the tetravalent oxide and for the studied solid solutions show that the extended Dulong and Petit law in Neumann–Kopp rule is verified for zirconia and the quaternary compounds. The Debye temperature of zirconia (590 K) and its yttria, erbia and ceria doped solid solutions (575–625 K) derived from these C_P measurements between 150 and 823 K is discussed and compared with that reported for other tetravalent metal oxides.

Keywords: Zirconia; Differential scanning calorimetry; Heat capacity; Debye temperature; Nuclear fuel

---

1. Introduction

Among the properties studied in the research and development programs concerning yttria stabilised zirconia, e.g. $Y_{0.2}Zr_{0.8}O_{1.9}$ and its application as advanced inert matrix fuels, e.g. $Er_{0.048}Y_{0.138}Pu_{0.086}Zr_{0.728}O_{1.907}$, the study of specific heat is of safety relevance interest. Specific heat capacity has been the subject of theoretical and experimental studies for classical nuclear fuels and for new fuels implying dissolution of fissile oxides in solid solution materials as it is for a zirconia based inert matrix fuel. Such a fuel could be used to eliminate excess plutonium while producing energy [1].

Determination of molar heat capacity (C_P^M) is required on one side to calculate the thermal conductivity from the thermal diffusivity of the material [2] and to calculate the enthalpy of the fuel. Thermal conductivity is a safety relevant parameter, which allows fuel temperature calculation in normal reactor operation conditions. Knowledge of C_P^M is also necessary to predict fuel behaviour in reactor transients. Large C_P^M values imply significant amounts of stored energy, and potential temperature increase for low thermal conductivity material [3].

Calculations of C_P^M may be performed applying Einstein [4] or Debye [5] model. The later is however more complete to describe capacity change over a large temperature range. This later model allows also determination of a material specific parameter: the Debye temperature T_D. Debye temperature is an important parameter that appears in the temperature dependent factor of the thermal conductivity [6].

---

[*] Corresponding author. Tel.: +41-56-310-4176; fax: +41-56-310-2203.
E-mail address: claude.degueldre@psi.ch (C. Degueldre).

0040-6031/03/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0040-6031(03)00060-1

This paper revisits the theory of specific heat of un-doped ZrO_2 and doped (i.e. $Y_{0.2}Zr_{0.8}O_{1.9}$ and $Er_{0.05}Y_{0.10}Ce_{0.10}Zr_{0.75}O_{1.925}$) zirconia that can be utilized as an analogous of an advanced inert matrix fuel of formula $Er_{0.048}Y_{0.138}Pu_{0.086}Zr_{0.728}O_{1.907}$ [1]. Comparison with UO_2 and with other tetravalent oxides is made in the discussion.

2. Theory

The molar heat capacity is derived from the energy of 1 mol of substance: $U^M = 3nN_AkT$ (J mol^{-1}) where n is the number of atom per molecule, N_A the Avogadro constant and k the Boltzmann constant. When energy is absorbed, if temperature changes, the specific heat at constant volume may be defined as follow: $C_V^M = (\delta U^M/\delta T)_V$ (J K^{-1} mol^{-1}). Combining these equations yields to the Neumann–Kopp rule [7]:

$$C_V^M = 3nN_Ak \quad (1)$$

or for elementary material ($n = 1$) leads to also a temperature independent value $C_V^M = 3nN_Ak$ known as Dulong and Petit law [8]. In a triatomic lattice like MO_2, this gives $C_V^M = 9nN_Ak$ with a specific heat capacity of 74.7 J K^{-1} mol^{-1}. This rule may be extended to 1 mol of a solid solution: $M_{1\xi 1}M_{2\xi 2}\ldots M_{i\xi i}\ldots M_{j\xi j}\ldots M_{z\xi z}O_{(2-1/2\Sigma\xi i+1/2\Sigma\xi j)}$, with ξ the stoechiometric coefficients, $\Sigma\xi = 1$ and M_z(IV), M_i(III) and M_j(V). However, as a consequence of Neumann–Kopp law, the comparable C_V^M values are given by: $C_V^{M*} = 3C_P^M(2 - 1/2\Sigma\xi i + 1/2\Sigma\xi j)^{-1}$.

The simple model of harmonic oscillator is unable to explain the specific heat at low temperature. However, Debye model based on quantum theories of lattice properties may be used. A Debye temperature T_D is defined above which all modes begin to be excited, and below which modes begin to be “frozen out”. C_V^M may be written as a function of T and T_D as follow:

$$C_V^M = 9Nk\left(\frac{T}{T_D}\right)^3 \int_0^{T_D/T} \frac{x^4e^x}{(e^x-1)^2}\,dx \quad (2)$$

with $N = nN_A$. Experimental determination of the isocore molar heat capacity is experimentally less easy than the isobar values. The later is defined as $C_P^M = (\delta H^M/\delta T)_P$, where H^M is the molar enthalpy given by $H^M = U^M + PV^M$. The difference between C_P^M and C_V^M can be derived from the basic thermodynamic relationship: $C_P^M = C_V^M + V^M(\alpha^2/\gamma)\,T$, where C_V^M is calculated by Eq. (2), $\alpha = (\delta V/\delta T)_P/V$ is the isobar coefficient of linear thermal expansion (K^{-1}), and $\gamma = -(\delta V/\delta P)_T/V$ isothermal compressibility (Pa^{-1}) and V^M the molar volume of the substance (m^3 mol^{-1}).

At higher temperature, additional increases of C_P^M result from lattice defects, electronic excitations and an harmonicity. Specific heat increases together with the increases of lattice defects which concentration increases at high temperature (between T_D and T_M, with T_M the melting temperature). This is observed for UO_2 as well as for ZrO_2. This anomaly has been discussed widely, e.g. [9], however these authors conclude that further efforts are required to understand this behaviour.

The isobaric molar specific heat may obtained combining Eq. (2) and the term $V^M(\alpha^2/\gamma)T$. A C_P^{M*} may also be defined for comparison with the C_P^M of MO_2.

3. Experimental

3.1. Material production and characterization

The preparation of all zirconia based material was carried out at PSI by the wet route because it yields a large material density [10]. All solutions were prepared by mixing nitrate solution of each element (Zr, Y, Er, and Ce) composing the final product. The starting compounds, zirconyl nitrate (purum, Fluka^{TM}), erbium and yttrium nitrate (puriss, Fluka^{TM}), and diammonium cerium hexanitrate were diluted separately in (Milli Q^{TM}) ultrapure water and mixed together to result in a solution with the required concentrations co-precipitation was carried out by adding ammonia under strong stirring. The precipitate was filtered on paper filter and washed 10 times with ultrapure water. The filtered phase was contacted with alcohol and milled utilizing a Retch unit with zirconia container and bowls. The wet powder was then dried for 24 h at 420 K. The dried powder was then manually desegregated prior calcination for 5 h at 900 K. The calcinated powder was milled again utilizing the Retch unit with zirconia vessel. The final powder was then pressed with 700 MPa during 1 min, two different brands of pellets were produced with 5 mm in diameter. Pelletized samples were then sintered in an oven with a temperature program including a first step at 1475 K for 4 h followed by a final step of 48 h at 1875 K. For the plutonia doped sample the preparation was performed by applying a dry route using an attrition-milling unit adapted to the zirconia material [11] starting with the powder of the oxide constituents.

The sintered pellets were cut to dimension of 1 mm thickness and 5 mm diameter with masses of the order of 110 ± 0.05 mg. The cutting was performed by a diamond saw. These disks were used to measure the heat capacity of the different compositions. The experimental sample density (ρ) of the disks used was determined by measuring the sizes (diameter and thickness) and weight utilizing a Mettler balance (AG204). The theoretical density (ρ_0 about 6 g cm^{-3}) was obtained from lattice parameter (a) gained by XRD (Phillips diffractometer PW1710, precision on $a \pm 0.001$ Å) measurements carried out on crushed materials. The relative densities ($\rho_\infty \rho_0^{-1}$) of the samples vary from about 0.85 to 0.95. For the plutonia doped sample the characterisation was also performed by XRD [12] confirming the quality of the material.

3.2. Calorimetry

At the University of Geneva, a Seiko 220 DSC unit was used for differential scanning calorimetry (DSC) measurements. The output signal is recorded as a raw data set. It must be evaluated using a separate computer unit with the calculation method. Sapphire was used for calibration. It was measured to control the reliability of the equipment. The parameters used for the DSC measurements were the following.

Temperature range	128–823 (±0.5) K
Temperature program	15 min at 128 (±0.5) K 1 K min^{-1} up to 133 (±0.5) K 15 min at 133 (±0.5) K 10 K min^{-1} up to 823 (±0.5) K

All measurements were carried out from 128 to 823 (±0.5) K using nitrogen (N_2: 99.995%, 1 bar) as gas flow and liquid nitrogen as a coolant for the low temperature. The samples were putted into an aluminium pot with cover. The sample containing pot-cover unit was tighten by a manual press to assure a good thermal contact of the unit. The prepared samples were positioned manually on the sample holder. A reference sapphire sample with similar dimensions like the other pellets and the specific heat capacity was also in the same range as the zirconia samples. In these conditions the precision on the C_P values is better than 5%. For the plutonia doped sample, the measurements were performed in Ar using a Netzsch STA 409 C DSC unit up to 1573 K. A sapphire disc was also used as a reference. The C_P measurements were carried out under contract at the Institute for Transuranium elements, Karlsruhe.

4. Results and discussion

Thermodynamic measurements from the pellet samples were converted from heat capacities in molar heat capacities. For the samples doped with yttria, erbia and ceria, calculations from experimental values require hypothesis on the behaviour of the dopants in the solid solution. The solution is supposed to be ideal, consequently: $(\delta H^M/\delta x_i)_T = 0$ and $C_P^M = \sum x_i C_P^M i$.

An average molecular weight of mixed phase (solid solution) (M) may also be defined by $M = \sum x_i M_i$ where M is the average molecular mass, x_i the fraction of i for 1 mol of solid solution and M_i the molecular mass of the component i. For the studied compounds, it is respectively: 123.2 for ZrO_2, 121.2 for $Y_{0.20}Zr_{0.80}O_{1.9}$, 130.5 for $Er_{0.05}Y_{0.10}Ce_{0.10}Zr_{0.75}O_{1.925}$ and 137.8 for $Er_{0.048}Y_{0.138}Pu_{0.086}Zr_{0.728}O_{1.907}$.

The molar heat capacities of zirconia, yttria stabilized zirconia and the latter doped with erbia and ceria or plutonia are reported as a function of temperature in Fig. 1. They are compared with data extracted from the literature [13–20] and corrected from the stoechiometry ($n = 3$). It must be noted that the measured capacities are C_P values and that the modelled values are C_V data. The correction factor is estimated in Table 1. Clearly the correction is small (<0.5 J K^{-1} mol^{-1} for temperature ranging from 150 to 820 K extended to 1400 K for the plutonia doped sample) and does not affect significantly the accuracy of the data, which range from 40 to 80 J K^{-1} mol^{-1}. Fig. 1 shows that all samples reach a plateau with a specific heat capacity at about the theoretical value of 74.7 J K^{-1} mol^{-1} (for $n = 3$). These solid solutions could be in a first approximation considered as ideal solutions since δC_P values between experimental and

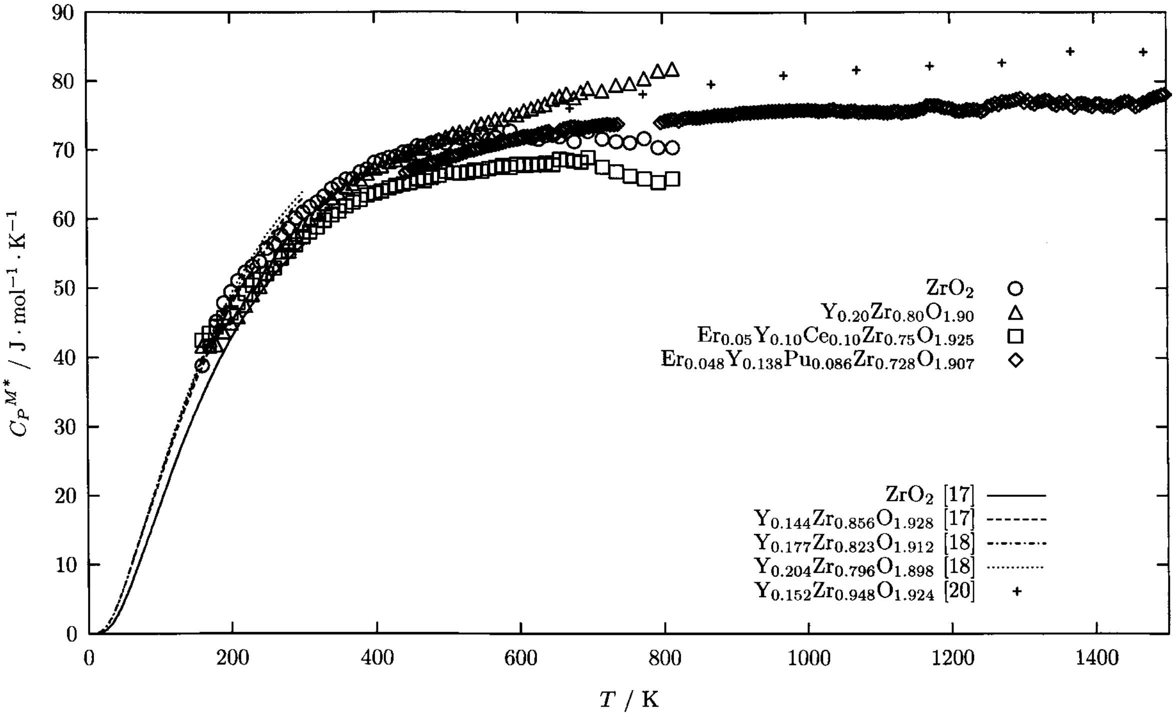

Fig. 1. Molar heat capacities of zirconia and, corrected for dioxide stoechiometry, yttria stabilized zirconia doped with erbia and ceria or plutonia as a function of temperature.

theoretical data are rather small, while distortions in the lattice of the zirconia solid solutions are identified [21]. However, it must be noted that there are slight differences between the curves. That relative for example to the sample $Y_{0.2}Zr_{0.8}O_{1.9}$ presents a slight increase above the Debye plateau that could be ascribable to lattice defects for this sample or that studied by Leclercq et al. [20]. In this case a correction by $\Delta C_P^M = (\zeta E_D/RT^2)e^{(-E_D/RT)}$ (with E_D the activation energy of the defects and ζ their fraction) suggested see [9] may be applied to model the increase of C_P^M on the Debye plateau. However, tests with this equation could not yield any reasonable values of E_D.

The temperature dependence of the molar heat capacity of the zirconia sample was normalized for a theoretical plateau value of a triatomic ($n = 3$) molecular material. Fig. 2 shows the plot of the normalized molar heat capacity of monoclinic zirconia with the absolute temperature normalized with zirconia Debye temperature. In the experimental temperature range of 150–800 K, the best fit for zirconia was obtained for $T_D = 590 \pm 10$ K. Similar plots may be obtained for the doped zirconia samples.

Table 2 presents Debye temperatures obtained so far for similar samples but determined by neutron diffraction [25,26]. It is noted that the Debye temperature

Table 1
Relevant macroscopic physical properties used for the correction of C_P in C_V

Material (MO_2)	α (10^6 K^{-1})	γ (10^{12} Pa^{-1})	V_M (10^6 m^3 mol^{-1})	V_M $(\alpha^2\gamma^{-1})T$ (J K^{-1} mol^{-1})[a]
ZrO_2	8.8–10.1[a]	5.6	21.8	0.35
UO_2	9.4–12.3[a]	4.8	24.6	0.62

[a] At 1000 K, data from [23,24].

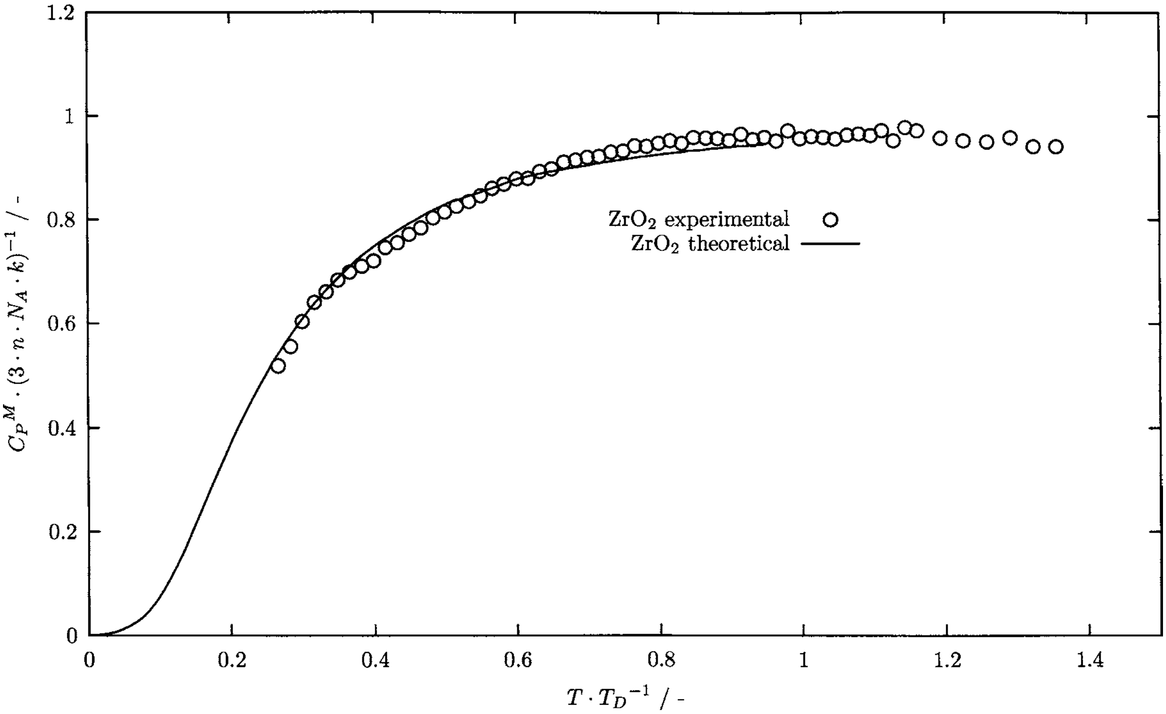

Fig. 2. Comparison of experimental and theoretical molar heat capacity values of ZrO_2 ($n = 3$) normalized by its theoretical values vs. the temperature normalized for $T_D = 590$ K.

values reported by these authors are different from the data determined in this work. Our data are, however, in between the data reported by these authors. The temperature ranges for which T_D values are determined are reported. It should however be noted that Debye temperatures are depending on the model conditions used, and that authors currently report temperatures ranging from 400 to 900 K.

Debye temperature results for zirconia may be compared for others tetravalent oxide materials. Table 3 presents a comparison of T_D values for several compounds from a same type, e.g. MO_2. The comparison may be complemented by using the relation between Debye temperature T_D and the melting temperature T_M suggested by Lindenmann [22]:

$$T_D = \frac{c\, T_M^{1/2}}{M^{1/2} V_M^{1/2}} \quad (3)$$

The c values, calculated for T_D, T_M, M and V_M reported in the literature, are given in Table 3 for comparison. The c value for TiO_2 (which exists under

Table 2
T_D for zirconia samples and from various studies

Material	T_D (K)	T_i–T_f (K)	Remark	Reference
ZrO_2	590 ± 20	150–800	Calorimetry	This work
ZrO_2	575	3–350	Calorimetry	[14]
$Y_{0.091}Zr_{0.909}O_{1.955}$	527 ± 20	15–1323	Neutron diffraction	[25]
$Y_{0.086}Zr_{0.914}O_{1.957}$	963	4–1923	Neutron diffraction	[26]
$Y_{0.20}Zr_{0.80}O_{1.90}$	575 ± 50	150–800	Calorimetry	This work
$Er_{0.05}Y_{0.10}Ce_{0.10}Zr_{0.75}O_{1.925}$	625 ± 50	150–800	Calorimetry	This work

Conditions: T_i–T_f studied temperature range.

Table 3
Relevant thermodynamic properties used for testing Lindenmann equation

Material	T_M (K)	V_M (cm^3 mol^{-1})	M (g mol^{-1})	T_D (K)	c (K$^{1/2}$ g$^{1/2}$ cm$^{3/2}$ mol^{-1})
TiO_2[a]	2383	18.7	79.9	943	746
ZrO_2[b]	2988	21.8	123.2	590	557
$Y_{0.2}Zr_{0.8}O_{1.9}$[c]	3075	21.6	121.2	575	531
CeO_2[c]	3003	24.1	172.1	410	481
ThO_2[c]	3573	26.8	264.0	393	553
UO_2[c]	3120	24.6	270.0	280	415

Data from [21,27,28].
[a] Tetragonal.
[b] Monocline.
[c] Cubic.

several allotropic forms) is relatively larger than the other, however the T_D value estimated for an average c values (e.g. 550 K$^{0.5}$ g$^{0.5}$ cm$^{1.5}$ mol^{-1}) would be about 650 K. The T_D decrease with increase of atomic number of the tetravalent cation is consequent of its increases of size. Since the T_D value for UO_2 is smaller than for ZrO_2, the C_P^M values reach faster the Debye plateau for UO_2 than for ZrO_2.

5. Concluding remarks

Progress in the understanding of basic thermodynamic properties of zirconia and zirconia based solid solutions has been achieved. C_P^M values of zirconia and its solid solutions with yttria, erbia and ceria or plutonia as dopants were measured from 128 to 1500 K. They follow the Debye model and the plateaus reach Dulong and Petit law extended in Neumann–Kopp rule for poly-atomic compounds and tested in this work for solid solution materials. These solid solutions may be in a first approximation considered as ideal solutions. Debye temperature T_D of the studied samples (575–625 K) are compared with other tetravalent oxides. T_D decreases with the atomic mass of the cations. These data can be used to quantify the behaviour of the materials as an advanced inert matrix fuel in nuclear reactors.

Acknowledgements

These tests were performed in the frame of the AFC program at the Paul Scherrer Institute led by Dr. Ch. Helwig who is acknowledged for his interest in this work. A plutonia doped sample produced at the Paul Scherrer Institute was measured under order No.: E 558359 at the Institute for Transuranium Elements, Karlsruhe, where Drs. C. Ronchi and M. Sheindlin are thanked for their collaborative work.

References

[1] C. Degueldre, U. Kasemeier, F. Botta, G. Ledergerber, Mater. Res. Soc. Symp. Proc. 412 (1995) 15.
[2] W. Parker, R. Jenkins, C. Butler, G. Abott, J. Appl. Phys. 32 (1961) 1679.
[3] D.R. Olander, Fundamental Aspects of Nuclear Reactor Fuel Elements, Report No. TID-26711-P1, Technical Information Center, Office of Public Affairs, Energy Research and Development Administration, Oak Ridge, TN, USA, http://plutonium-erl.actx.edu/fanrfe.html, 1976.
[4] A. Einstein, Ann. Phys. 34 (1911) 170, and errata 590.
[5] P. Debye, Ann. Phys. 39 (1912) 789.
[6] R. Gibby, J. Nucl. Mater. 38 (1971) 163.
[7] F.E. Neumann, Ann. Phys. 99 (1831) 9;
H. Kopp, Ann. Chem. Pharm. Suppl. 3 (1864) 289.
[8] P. Dulong, A.T. Petit, Ann. Chim. Phys. 10 (1819) 395.
[9] K. Ranta-Puska, Specific Heat of UO_2 and MOX Fuel: A Literature Review, OECD Halden Reactor Project, Paris, 1998.
[10] Y.W. Lee, H.S. Kim, S.H. Kim, C.Y. Joung, S.H. Na, G. Ledergerber, P. Heimgartner, M. Pouchon, M. Burghartz, J. Nucl. Mater. 274 (1999) 7.
[11] G. Ledegerber, C. Degueldre, P. Heimgartner, M. Pouchon, U. Kasemeyer, Progr. Nucl. Energy 38 (2001) 301.
[12] M. Burghartz, G. Ledegerber, F. Ingold, P. Heimgartner, C. Degueldre, Prog. Nucl. Energy 38 (2001) 247.
[13] S. Tatsuya, T. Atake, T. Mori, H. Yamamura, Solid State Ionics 79 (1995) 143.
[14] M.V. Nevitt, Y. Fang, S.-K. Chan, J. Am. Ceram. Soc. 73 (1990) 2502.

[15] T. Shirakami, T. Tojo, T. Atake, T. Mori, H. Yamamura, Thermochim. Acta 267 (1995) 415.
[16] T. Tojo, T. Atake, T. Shirakami, T. Mori, H. Yamamura, Solid State Ionics 86–88 (1996) 89.
[17] T. Tojo, T. Atake, T. Mori, H. Yamamura, J. Chem. Thermodyn. 31 (1999) 831.
[18] T. Tojo, T. Atake, T. Mori, H. Yamamura, J. Therm. Anal. Calorim. 57 (1999) 447.
[19] S. Raghavan, H. Wang, R.B. Dinwidie, W.D. Porter, M.J. Mayo, Scr. Mater. 39 (1998) 1119.
[20] B. Leclercq, R. Mévrel, V. Liedtke, W. Hohenauer, in: Proceedings of the Second Meeting on Space and Aerospace Materials Technology, AMTT, Seibersdorf, 4 November 2002.
[21] P. Villella, S.D. Conradson, F.J. Espinosa-Faller, S.R. Foltyn, K.E. Sickafus, J.A. Valdez, C.A. Degueldre, Phys. Rev. B 64 (2001) 104101.
[22] F.A. Lindenmann, Phys. Z 11 (1910) 609.
[23] M. Iridi, PhD Thesis, Uni. Fourier, Grenoble, France.
[24] Handbook of CRC Materials Science and Engineering, p. 511.
[25] D.N. Argyriou, J. Appl. Crystallogr. 27 (1994) 155.
[26] E. Kisi, M. Yuxiang, J. Phys. 10 (1998) 3823.
[27] http://www.oxmat.co.uk.
[28] http://www.insc.anl.gov.