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Journal of Nuclear Materials 319 (2003) 6–14

journal of nuclear materials

www.elsevier.com/locate/jnucmat

Thermal conductivity of zirconia based inert matrix fuel: use and abuse of the formal models for testing new experimental data

C. Degueldre [a,*], T. Arima [b], Y.W. Lee [c]

[a] Laboratory for Materials Behaviour, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland
[b] Institute of Environmental Systems, Kyushu University, 812-8581 Fukuoka, Japan
[c] Korean Atomic Energy Research Institute, 305-600 Taejon, South Korea

Abstract

An inert matrix fuel material based on yttria-stabilized cubic zirconia: $Er_xY_yPu_zZr_{1-x-y-z}O_{2-(x+y)/2}$ ($x+y=0.15$, z: [0.05–0.15]) was proposed for burning excess plutonium in light water reactors. The studied inert matrix fuel is made of cubic stabilized zirconia. The limited number of experimental thermal conductivity data justifies this formal and intensive study. Approaches derived from Klemens theory were revisited and the derived conductivity model applied for zirconia, accounting the effects of phononic scattering centers. The hyperbolic thermal conductivity trend with temperature known for pure zirconia, is reduced by isotopes, impurities, dopants and oxygen vacancies, which act as scattering centers and contribute to conductivity reduction to a flat plot with temperature for stabilized zirconia. It is experimentally observed that the thermal conductivity derived from laser flash measurements for $Er_xY_yM_zZr_{1-x-y-z}O_{2-(x+y)/2}$ (with M = Ce or Pu, $z=0$ or ~ 0.1 and $x+y=0.15$) is rather constant as a function of temperature in the range 300–1000 K. The thermal conductivity was observed to depend on the concentration of dopants such as $YO_{1.5}$ and/or $ErO_{1.5}$, CeO_2 (analogous of PuO_2) or PuO_2. The bulk material conductivity of $Er_{0.05}Y_{0.10}Pu_{0.10}Zr_{0.75}O_{1.925}$ is about 2 $W\,m^{-1}\,K^{-1}$. In this study, the thermal conductivity data of both monoclinic and stabilized cubic zirconia based IMF are tested with the model approach in order to understand the experimental data in a semi-quantitative way.

1. Introduction

Zirconia based inert matrix fuels (IMFs) are likely to be an attractive fuel candidate for burning excess plutonium in light water reactors. An IMF material based on yttria-stabilized cubic zirconia $Y_yZr_{1-y}O_{2-y/2}$ has been proposed by the author [1]. Such a cubic zirconia has high melting point, low neutron capture cross-section, compatibility with cladding, and good behaviour under irradiation. Y_2O_3 acts as a stabilizer and Er_2O_3 is suggested as additional stabilizer and as a burnable poison. As a result, the composition of the cubic zironia IMF is $Er_xY_yPu_zZr_{1-x-y-z}O_{2-(x+y)/2}$ (with $x+y \sim 0.15$) [1].

The thermal conductivity is one of the most important properties of nuclear fuels. For the cubic stabilized zirconia as an IMF, a limited number of experimental thermal conductivity data are available, but intensive studies are in progress at the Paul Scherrer Institute [2] and at the Japanese Atomic Energy Research Institute [3]. Such data suggests that the thermal conductivity of these yttria-stabilized zirconia does not depend on temperature in the 300–1000 K range but depends on the concentration of dopants such as $YO_{1.5}$ and/or $ErO_{1.5}$, CeO_2 (analogous of PuO_2) or PuO_2. The measurements

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[*] Corresponding author. Tel.: +41-56 3104176; fax: +41-56 3102203.
E-mail address: claude.degueldre@psi.ch (C. Degueldre).

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doi:10.1016/S0022-3115(03)00127-2

of thermal conductivity have been performed for $Er_xY_yM_zZr_{1-x-y-z}O_{2-(x+y)/2}$ (with M = Ce or Pu, $z = 0$ or ~ 0.1 and $x + y \sim 0.15$). In this study, the thermal conductivity of both monoclinic and stabilized cubic zirconia is reconsidered in terms of formulation and dataset based on calculation, and its dependence on composition is discussed. Since the thermal conductivity depends on macroscopic imperfections such as pores, fissures, and microscopic or lattice defects, the modeling can be split into the corresponding parts. The porosity part may be accounted for example by the Loeb approximation. The model for the lattice thermal conductivity is based on the Debye–Einstein theory of ionic dielectics, and the Klemens approach for the heat conductance [4]. The model considered phonon scattering by matrix isotopes, impurities, dopants or additives and oxygen vacancies randomly dispersed. The model testing takes into account the recent values of the Debye temperature measured for the considered phases [5]. The approach is based on the previous studies such as the calculation method adapted by Fukushima et al. [6] for $(Ln,Pu,U)O_{2-\xi}$ solid solutions, where Ln is the lanthanide ion. This approach tested to calculate the thermal conductivity of $(Ln,Y,An,Zr)O_{2-\xi}$ solid solution, where An is the actinide ion, based on that of $Y_yZr_{1-y}O_{2-y/2}$ cubic zirconia, itself based on ZrO_2 data. The thermal conductivity model is tested for stabilized cubic zirconia doped with PuO_2 as a function of the temperature.

2. Review of relevant studies on thermal conductivity of mixed oxides

It is useful to revise the formulation [4] and the dataset used in order to perform the thermal conductivity calculation for MO_2 and mixed oxides. In general, the thermal conductivity κ of solid is given for a Debye dielectric solid by

$$\kappa = \frac{1}{A + B \cdot T} = \frac{1}{W_l + W_p}, \qquad (1)$$

where A and B are constants. The constant A ($= W_l$) corresponds to the thermal resistivity caused by the phonon–lattice defect interactions. The term of $B \cdot T$ ($= W_p$) corresponds to phonon–phonon interactions (Umklapp process).

2.1. Modeling the effect of temperature

The intrinsic lattice resistivity W_p of dielectric solids can be estimated from the following relationship [7,8]:

$$W_p = B \cdot T = \frac{\gamma^2 \cdot T}{\left(\frac{24}{10}\right) \cdot 4^{1/3} \cdot \left(\frac{k_B}{h}\right)^3 \cdot \overline{M} \cdot \overline{V}^{1/3} \cdot T_D^3}, \qquad (2)$$

where k_B is the Boltzmann's constant, h the Plank's constant, $\overline{V}$ is the average atomic volume and $\overline{M}$ the average atomic mass. B can be calculated using Eq. (2) using both the Debye temperature T_D and the Grüneisen constant γ, which are two material related parameters.

Thus, the intrinsic thermal conductivity of MO_2 pure crystalline material follows an hyperbolic trend with the temperature. Both Debye temperature and Grüneisen constant values are two relevant data since they are to the power 3 and 2 in Eq. (2). In a metal dioxide there are two types of atomic masses and the mass ratio should satisfy the condition: $M_M/M_O < 4$ required to describe a Debye solid. The expression (2) in (1) may then reproduce the lattice conductivity of the ionic solid above the Debye temperature. However, to apply the theory, the free pathway l calculated from the formula

$$\kappa = 1/3 \cdot C_V \cdot \rho \cdot \bar{v} \cdot l \qquad (3)$$

with $\bar{v}$ the average phonon velocity, ρ the material density and C_V its specific isochor heat capacity, should be larger than the size of the scattering centers.

The intrinsic lattice resistivity of pure MO_2 may be completed by a lattice defect term.

2.2. Modeling the effect of point defects

The lattice defect thermal resistivity of dielectric solids is given by [9]

$$W_l = \frac{\pi^2 \cdot \overline{V} \cdot T_D}{3 \cdot \bar{v}^2 \cdot h} \sum_i \Gamma_i, \qquad (4)$$

where Γ_i is a scattering cross-section parameter of the phonons by point defect i (isotopes, impurities, dopants and oxygen vacancies) and is approximately given by [10]

$$\Gamma_i = x_i \cdot \left[\left(\frac{\overline{M} - M_i}{\overline{M}} \right)^2 + \varepsilon \cdot \left(\frac{\bar{r} - r_i}{\bar{r}} \right)^2 \right], \qquad (5)$$

where x_i and M_i are the atomic fraction and the mass of the point defect i, respectively, $\overline{M}$ the average atomic mass of the host lattice site, r_i the atomic (ion) radius of the point defect i in its own lattice, $\bar{r}$ the average atomic radius of the compounds of host lattice and ε a parameter representing the magnitude of the lattice strain generated by the point defect. Abeles [10] explains that ε should be regarded as a phenomenological, adjustable parameter.

Fukushima et al. [6] divided the term of W_i into two items caused by different defects. It can be written as

$$W_l = W_l(0) + \Delta W_l(x), \qquad (6)$$

where $W_l(0)$ is caused by the defects such as impurities included in the sample, and $\Delta W_l(x)$ is the additional one caused by interactions of solutes. According to Eq. (4), $\Delta W_{\mathrm{I}}(x)$ can be expressed as follows:

$$\Delta W_{\mathrm{I}}(x) = C \cdot \Delta\Gamma, \tag{7}$$

where

$$C = \frac{\pi^2 \cdot \overline{V} \cdot T_{\mathrm{D}}}{3 \cdot \bar{v}^2 \cdot h} \tag{8}$$

and $\Delta\Gamma$ is a difference between the value of $\sum \Gamma_i$ for the solvent and that for the solid solutions. It is necessary to estimate T_{D} and $\bar{v}$ for solid solutions to calculate the lattice defect thermal resistivity.

2.3. The intrinsic lattice resistivity: comparing the models

The intrinsic lattice resistivity of dielectric solids applied by Gibby [8] is inspired by Leibfried–Schömann work [7]. Using Eq. (2), the intrinsic thermal conductivity $\kappa_{i_{\mathrm{Gibby}}}$ can be written as

$$\kappa_{i_{\mathrm{Gibby}}} = \frac{\left(\frac{24}{10}\right) \cdot 4^{1/3} \cdot \left(\frac{k_{\mathrm{B}}}{h}\right)^3 \cdot \overline{M} \cdot \overline{V}^{1/3} \cdot T_{\mathrm{D}}^3}{\gamma^2 \cdot T}. \tag{9}$$

The Grüneisen parameter γ can be expressed by the following relation,

$$\gamma = \frac{V_{\mathrm{M}} \cdot B_T \cdot \beta}{C_V} = \frac{3 \cdot V_{\mathrm{M}} \cdot B_T \cdot \alpha}{C_V},$$

where $\beta = 3 \cdot \alpha$, and V_{M} is the molar volume, B_T the bulk modulus, β the coefficient of volumetric thermal expansion and α the coefficient of linear thermal expansion.

An alternative to Eq. (9) was proposed by Klemens [11,12]. According to his formulation, the intrinsic thermal conductivity becomes

$$\kappa_{i_{\mathrm{Klemens}}} = \left(\frac{3}{2 \cdot \gamma^2}\right) \cdot \left(\frac{\mu \cdot v^2}{N \cdot \omega_m}\right) \cdot \frac{1}{T}, \tag{10}$$

where μ is the shear modulus, v the transverse wave speed, N the number of atoms per molecule i.e. 3 for $\mathrm{MO_2}$, ω_m the Debye frequency of the acoustic branch. It is given by $\omega_m = \omega_{\mathrm{D}}/N^{1/3}$, where ω_{D} is the 'per atom' Debye frequency. Furthermore, the relation between Debye temperature and ω_{D} is written as $T_{\mathrm{D}} = h \cdot \omega_{\mathrm{D}}/(2 \cdot \pi \cdot k_{\mathrm{B}})$.

Thus, if the transverse wave speed can be calculated, the intrinsic thermal conductivity may be derived. Based on the elasticity theory, the transverse wave speed of phonon is given by $v = \sqrt{\mu/\rho}$. Consequently, both shear modulus and Debye temperature are required to calculate Eq. (10).

The intrinsic thermal conductivities from both approaches should be formally equal since these expressions are derived for perfect dielectric solids. The relation between the Debye temperature and the average phonon velocity is given by the Debye approximation $\bar{v} = ((2 \cdot \pi \cdot k_{\mathrm{B}} \cdot T_{\mathrm{D}})/h) \cdot \delta/(6 \cdot \pi^2)^{1/3}$, where δ is the average size of the molecule and δ^3 the volume per molecule in the crystal. Focusing on difference in expression of sound velocity, Eqs. (9) and (10) are re-written as follows:

$$\kappa_{i_{\mathrm{Gibby}}} = \frac{0.30}{\gamma^2 T} \cdot \left(\frac{\overline{M}}{\overline{V}^{2/3}}\right) \cdot \bar{v}^3, \tag{11}$$

$$\kappa_{i_{\mathrm{Klemens}}} = \frac{0.27}{\gamma^2 T} \cdot \left(\frac{\overline{M}}{\overline{V}^{2/3}}\right) \cdot \left(\frac{v^4}{\bar{v}}\right), \tag{12}$$

where $\rho = \overline{M}/\overline{V}$. For $N = 3$, the ratio of $\kappa_{i_{\mathrm{Gibby}}}$ to $\kappa_{i_{\mathrm{Klemens}}}$ is given by

$$\frac{\kappa_{i_{\mathrm{Gibby}}}}{\kappa_{i_{\mathrm{Klemens}}}} = \frac{0.30 \cdot \bar{v}^4}{0.27 \cdot v^4}. \tag{13}$$

If the transverse wave speed is equal to that derived by Debye approximation, the difference between these thermal conductivities is estimated to be 10%.

3. Applying the models for zirconia and comparing literature data

The dataset for zirconia used in the thermal conductivity calculations are given in Table 1. Some values given for monoclinic zirconia are less accurate since the material is non-stabilized, not always ultra-pure or defect-free. It must be remembered that any thermal treatment above 1420 K yields phase transition. The monoclinic unit cell ($a = 514.6$ pm, $b = 521.3$ pm, $c = 531.1$ pm, $\beta = 99.2°$) passes then in a tetragonal cell ($a = 515$ pm, $c = 527$ pm), which undergoes contraction from a unit cell volume of 0.1407–0.1397 $\mathrm{nm^3}$ for the monoclinic and tetragonal phases respectively. This phase transition limits the preparation of non-stabilized monoclinic zirconia. This also justifies the difficulty to produce or find the pure defectless material. Consequently, monoclinic zirconia samples are unlikely defect free. The distortions in the lattice as identified by EXAFS e.g. [13] yield phonon scattering centers and affect all thermo-plastic properties.

3.1. Conductivity calculation for monoclinic zirconia

3.1.1. The case of pure monoclinic zirconia

The thermal conductivity data from the literature for monoclinic zirconia are summarized as follow. For a sample of one grain of non-stabilized zirconia the measure by Bisson et al. [16] gave 8.1 $\mathrm{W\,m^{-1}\,K^{-1}}$ at RT. For nano-particle material sintered at low temperature the conductivity measured by Raghavan et al. [17] was 6 $\mathrm{W\,m^{-1}\,K^{-1}}$ at RT and about 3.7 $\mathrm{W\,m^{-1}\,K^{-1}}$ at 1000 K, corresponding to $A = 9.87 \times 10^{-2}$ $\mathrm{m\,K\,W^{-1}}$ and $B = 1.81 \times 10^{-4}$ $\mathrm{m\,W^{-1}}$. A sample of non-stabilized zir-

Table 1
Dataset for macroscopic properties of zirconia

Parameter	Symbol	Unit	Value for ZrO_2 (*m*)	Values for $(Y,Zr)O_{2-\xi}$[a](*c*)	Ref.
Molecular weight	M	$kg\,mol^{-1}$	123.22×10^{-3}	121.55×10^{-3}	[14]
Density	ρ	$kg\,m^{-3}$	5.85×10^{3}	5.95×10^{3}	[14]
Molar volume	V_M	m^3	21.06×10^{-6}	20.43×10^{-6}	[14]
Average atomic volume	$\overline{V}$	m^3	1.166×10^{-29}	1.160×10^{-29}	[14]
Average atomic mass	$\overline{M}$	kg	6.82×10^{-26}	6.90×10^{-26}	[14]
Linear thermal expansion coefficient	α	K^{-1}	10×10^{-6}	10×10^{-6}	[21]
Isochor molar heat capacity	C_V	$J\,mol^{-1}\,K^{-1}$	74.7[b]	72.8[b]	[5]
Debye temperature[c]	T_D	K	590 ± 20	575 ± 50	[5]
Shear modulus	μ	Pa	83×10^{9}	79×10^{9}	[24,36]
Bulk modulus	B_T	Pa	201×10^{9}	145×10^{9}	[24,36]
Grüneisen constant	γ	–	2.0[d]	1.4	[24]

[a] e.g. for $Y_{0.15}Zr_{0.85}O_{1.925}$.

[b] Theoretical value on Debye plateau.

[c] Note: T_D data are model and temperature dependant e.g. Tojo et al. [15] $T_D = 400$–700 K.

[d] Calculated for $B_T = 201$ GPa.

conia with high density of dislocations and grain boundaries (with 0.9 theoretical density (TD), and impurities e.g. 2 mol% Hf) was measured by Pouchon et al. [18], κ values of 2.7 $W\,m^{-1}\,K^{-1}$ are reported at RT. Previous studies on zirconia samples estimated κ of about 2 $W\,m^{-1}\,K^{-1}$ where its temperature dependence was relatively small [19], but, these values are for zirconia doped samples.

The intrinsic thermal conductivity given by Gibby's approach is estimated to be 30 $W\,m^{-1}\,K^{-1}$ at 500 K and 15 $W\,m^{-1}\,K^{-1}$ at 1000 K for B of 6.67×10^{-5} $m\,W^{-1}$. Presently, B is about three times smaller that expected. The Grüneisen parameter γ was 2.0 and the Debye temperature T_D was 500 K (average between our values and that of Tojo et al. [15]) for these calculations. Such a relatively large difference is caused by the difference in expression of phonon velocity. The results obtained by Klemens's method is influenced by the transverse wave speed of phonon. Calculations give v of 4200 $m\,s^{-1}$ using the shear modulus and the density of monoclinic zirconia and $\bar{v}$ of 6500 $m\,s^{-1}$ for T_D of 590 K. The intrinsic lattice resistivity of pure MO_2 may be corrected by the lattice defect term A, which would equal $8.53 \times 10^{-1} \times [0.536 + 3.7 \times 10^{-2}\,\varepsilon]$ $m\,K\,W^{-1}$. Clearly with $\varepsilon = 0$, A is still at least four times that determined experimentally. Similar discrepancies between experimental and theoretical A and B values are also reported for UO_2 and PuO_2 [6].

Simplifications and limitations on the use of the formal model must be pointed out, which makes discrepancies between experimental and theoretical values. The expression (2) in (1) can reproduce the lattice conductivity of the ionic solid above the Debye temperature. Application of these formulae are only valid for perfect crystals, which is far to be the case for monoclinic non-stabilized zirconia. In zirconium dioxide the mass ratio is $M_{Zr}/M_O \sim 5$, which does not fully satisfy the condition required for Debye solid. In Eq. (2) both Debye temperature and Grüneisen constant values are two relevant data since they are to the power 3 and 2. Finally, the phonon free pathway l calculated from Eq. (3) with $\kappa = 3$ $W\,m^{-1}\,K^{-1}$, $C_V = 480$ $J\,kg^{-1}\,K^{-1}$, $\bar{v} = 6000$ $m\,s^{-1}$ and $\rho = 5850$ $kg\,m^{-3}$, is ~0.5 nm and is of the same order as the size of the scattering centers, which makes application of Klemens theory somewhat inaccurate.

Anyway, in a prospective way, calculations are further carried out in order to assess the semi-quantitative application of the Eq. (1) for zirconia using with its intrinsic conductivity.

3.1.2. *Effect of lattice defects on thermal resistivity of monoclinic zirconia*

The lattice defect thermal resistivity can be expressed by Eqs. (4) and (5). As cited in Ref. [11], the defects scattering phonons should be considered to be the substituted atoms for host Zr atoms in a host lattice. For the case of pure monoclinic zirconia, such a lattice defect thermal resistivity is somewhat difficult to be calculated using Eqs. (4) and (5). Several studies introduced the constant term accounting for the thermal resistance resulting from the other defect sources such as impurities [4,9]. The introduced constant term was experimentally determined by the thermal conductivity of the host lattice such using the factor derived from Eq. (5). In order to calculate this term of monoclinic zirconia, more reliable data of thermal conductivity are needed. Since the thermal conductivity of monoclinic zirconia depends on temperature [12], it is determined by both A and B values in Eq. (1).

In order to investigate the effects of the lattice defects, the contribution of the zirconium isotopes is calculated.

The natural abundance of zirconium isotopes are 51.45%, 11.22%, 17.15%, 17.38% and 2.8% for ^{90}Zr, ^{91}Zr, ^{92}Zr, ^{94}Zr and ^{96}Zr, respectively. According to Eq. (5), the contribution from the isotopic variation is estimated to yield a Γ of 0.00034. The magnitude of this value is very small, say negligible. In this calculation, the contribution from the lattice strain is neglected.

Contamination with chemicals may contribute to the lattice defect thermal resistivity. Without zirconia specific purification, Hf contamination is of the order of the 1–2 mol%. The lattice defect thermal resistivity due to Hf contamination was estimated using Eq. (4) and (5) with $r_{\mathrm{Hf}}4+ = 78$ pm and $M_{\mathrm{Hf}} = 178.49$ g mol^{-1}. Also here, the lattice strain contribution is neglected. The C value of 0.818 m K W^{-1} for the monoclinic zirconia is used. The results are shown in Table 2.

The values of Γ and increase of thermal conductivity are almost proportional to the contamination of Hf. The contribution from the Hf contamination is much larger than that from isotopic effect of zirconium and is not negligible.

Table 2
Hf contribution on resistivity

Hf fraction mol%	Γ[a]	ΔW (m K^{-1} W^{-1})
0.0	0.000342	0.000280
0.5	0.004850	0.003970
1.0	0.009220	0.007540
1.5	0.013500	0.011000
2.0	0.017600	0.014400

[a] Without lattice strain effect.

3.2. Conductivity calculation for cubic zirconia

3.2.1. The case of pure cubic stabilized zirconia

As well known, addition of the 8 mol% Y_2O_3 in ZrO_2 fully stabilizes zirconia in a $(Y,Zr)O_{2-\xi}$ cubic phase (CSZ) at RT. Under the assumption that the thermal and mechanical properties are nearly equal for zirconia with 9.4–11.0 mol% Y_2O_3, the calculation of thermal conductivity can progress. The calculated thermal conductivity of $(Y,Zr)O_{2-\xi}$ may consequently be used for the $(Ln,Y,An,Zr)O_{2-\xi}$ solid solutions.

In order to calculate the intrinsic lattice thermal conductivity, the values of both γ and T_D for zirconia with ~10 mol% yttria are needed. Several researchers investigated the thermophysical and mechanical properties of CSZ [20–23]. Kisi and Yuxiang gives γ, μ and T_D values [24]. But the value of T_D is found to be higher than that obtained by other experiments. So the value of 527 K is chosen for moderate T_D [25]. Using $\gamma = 1.37$ [23] and $T_D = 527$ K [24], Gibby's approach gives B of 2.08×10^{-5} m W^{-1}. For the Klemens's theory, the value of B is estimated to be 1.70×10^{-4} m W^{-1} using μ of 79 GPa [23]. The relatively large difference is caused by the difference in expression of phonon velocity, as described in Section 2. The Klemens's approach gives the transverse wave speed of 3500 m s^{-1} while Gibby's approach gives the average phonon velocity of 5800 m s^{-1}.

The effect of grain size in polycrystalline material is supposed to have a marked effect on the conductivity. κ could theoretically be reduced vs its intrinsic values by 30–40% for 1 μm grains, 50% for 100 nm grains and 60% for 10 nm grains [26]. This effect is not treated in this paper since this correction is not verified experimentally e.g. [17]. This is justified since for stabilized zirconia Eq. (3) yields to a phonon pathway (~0.5 nm) of the order of the scattering center sizes (~0.2 nm), which are much smaller than the grain sizes.

3.2.2. Effect of lattice defects on thermal resistivity of cubic zirconia

In order to estimated the lattice defect thermal resistivity due to dopant atoms, the value of C has to be calculated. The C value can be calculated by Eq. (7). Using $T_D = 527$ K, the values of C are estimated to be 0.912 m K W^{-1} for $\bar{v} = 5800$ m s^{-1}.

The thermal resistivity caused by dopant atoms is given by Eq. (5). $\Delta\Gamma$ for $(Y,Zr)O_{2-\xi}$ solid solution is written:

$$\begin{aligned}\Delta\Gamma &= \left|\sum_i \Gamma_{i(\mathrm{ss})} - \sum_i \Gamma_{i(\mathrm{ZrO_2})}\right| \\ &= \left[\left|\frac{x_{\mathrm{Zr}}\cdot M_{\mathrm{Zr}}^2 + x_{\mathrm{Y}}\cdot M_{\mathrm{Y}}^2}{\overline{M}^2} - \frac{3\cdot M_{\mathrm{Zr}}^2}{(M_{\mathrm{Zr}}+2\cdot M_{\mathrm{O}})^2}\right| \right.\\ &\quad \left. + \left|\frac{x_{\mathrm{O}}\cdot M_{\mathrm{O}}^2}{\overline{M}^2} - \frac{6\cdot M_{\mathrm{O}}^2}{(M_{\mathrm{Zr}}+2\cdot M_{\mathrm{O}})^2}\right|\right] \\ &\quad + \varepsilon\cdot\left[\left|\frac{x_{\mathrm{Zr}}\cdot r_{\mathrm{Zr}}^2 + x_{\mathrm{Y}}\cdot r_{\mathrm{Y}}^2}{\bar{r}^2} - \frac{3\cdot r_{\mathrm{Zr}}^2}{(r_{\mathrm{Zr}}+2\cdot r_{\mathrm{O}})^2}\right|\right. \\ &\quad \left. + \left|\frac{x_{\mathrm{O}}\cdot r_{\mathrm{O}}^2 + x_{\mathrm{O_V}}\cdot r_{\mathrm{O_V}}^2}{\bar{r}^2} - \frac{6\cdot r_{\mathrm{O}}^2}{(r_{\mathrm{Zr}}+2\cdot r_{\mathrm{O}})^2}\right|\right], \end{aligned} \quad (14)$$

where the subscript (ss) means the solid solution, and O_V means the oxygen vacancy. To calculated the $\Delta\Gamma$, the ion mass and radius are needed. Table 3 shows the values of ion radius given by Shannon and Prewitt [27].

In order to determine the ion radius, the lattice parameter a for the cubic zirconia is used. Terblanche reported the relation between the lattice parameter and content of yttria as a function of temperature [28]. On the other hand, the diagonal of the cell for the cubic zirconia (fluorite structure) is given by e.g. [29]

$$\begin{aligned}\frac{\sqrt{3}}{4}\cdot a_{(\mathrm{Y,Zr})\mathrm{O}_{2-\xi}} &= 3\cdot x_{\mathrm{Zr}}\cdot r_{\mathrm{Zr}} + 3\cdot x_{\mathrm{Y}}\cdot r_{\mathrm{Y}} + \frac{3}{2}\cdot x_{\mathrm{O}}\cdot r_{\mathrm{O}} \\ &\quad + \frac{3}{2}\cdot x_{\mathrm{O_V}}\cdot r_{\mathrm{O_V}}. \end{aligned} \quad (15)$$

Table 3
Atomic radii r (pm) of the ion components as a function of coordination number (CN)

Ion	CN			
	4	6	7	8
Zr^{4+}	–	72.0	78.0	84.0
Y^{3+}	–	90.0	96.0	101.9
Er^{3+}	–	89.0	94.5	100.4
Ce^{4+}	–	87.0	92.0	97.0
Pu^{4+}	–	86.0	–	96.0
O^{2-}	136.4	–	–	–

Then, under the assumption that the radius of oxygen vacancy is equal for zirconia with 10–30 mol% Y_2O_3, the r_{O_V} is determined from fitting the lattice parameter given by Eq. (15) to the measured lattice parameter. For the hypostoichiometric oxide $(Y,Zr)O_{2-\xi}$, the mean CN of cations is 8–4. Considering the decrease of cation ion radius with decrease of CN, the radius of oxygen vacancy is estimated to be 176 pm.

The value of ε is determined as the adjustable parameter [8]. The thermal conductivities of cubic zirconia with 10–30 mol% yttria were measured by Degueldre et al. [3] and Pouchon et al. [2]. Fitting the data from these references for the thermal resistivity written by Eq. (14), the value ε of 10 ± 2 is obtained as an adjustable parameter. In Table 4, the scattering cross-sections and thermal resistivities due to added yttria are summarized. These thermal resistivities are calculated using $\varepsilon = 10.4$ and $C = 0.912\ \mathrm{m\,K\,W^{-1}}$.

Fig. 1 shows the thermal conductivities of cubic zirconia with 0–30 mol% Y_2O_3. This figure shows that the thermal conductivity of yttria-stabilized cubic zirconia is decreasing with the increase of yttria concentration.

Alternatively, the ε parameter may be evaluated using the following equation: $\varepsilon = 32 \cdot (1 + 1.6 \cdot \gamma)^2$ [9]. With $\gamma = 1.37$, a value of 326 is obtained for the strain parameter. This value is too large to express the thermal conductivity of yttria-stabilized cubic zirconia since the scattering cross-section parameters due to added yttria is not so small.

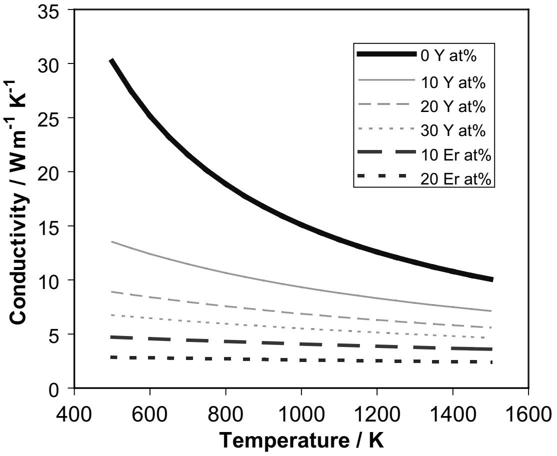

Fig. 1. Calculated intrinsic thermal conductivity of $Y_yZr_{1-y}O_{2-y/2}$ as a function of temperature. Conditions: Debye temperature T_D 500 K and the Grüneisen constant γ 2.1.

Fig. 2 shows the calculated thermal conductivities for yttria-stabilized zirconia doped with CeO_2 and PuO_2. These calculations are performed for the zirconia with additions of CeO_2 or PuO_2 yielding cubic phase material. In these calculations, the thermal conductivity of $Y_{0.1}Zr_{0.9}O_{1.95}$ as intermediate material was used, and the valence of Pu and Ce ions is assumed to be +4. In Table 5, the scattering cross-sections and thermal resistivities due to added CeO_2 and PuO_2 are summarized. These thermal resistivities are calculated using $\varepsilon = 10.4$ and $C = 0.912\ \mathrm{m\,K\,W^{-1}}$. Both thermal conductivities of cubic zirconia added with CeO_2 or PuO_2 decreases when increasing their concentration. A stronger decrease of thermal conductivity is observed for the cubic zirconia by adding PuO_2 compared to that obtained by adding CeO_2. This is the reason why the contribution to the thermal resistivity is larger for heavier atomic mass also enhancing the scattering cross-section.

Table 4
The scattering cross-sections $\Delta\Gamma_M$ (M = mass) and $\Delta\Gamma_r$ (r = radius) and thermal resistivities $\Delta W = C \cdot (\Delta\Gamma_M + \varepsilon \cdot \Delta\Gamma_r)$ due to yttria fraction

Cubic zirconia	$\overline{M}$ (g mol^{-1})	$\bar{r}$ (pm)	$\Delta\Gamma_M$	$\Delta\Gamma_r$	ΔW (m K W^{-1})
ZrO_2	41.073	118.9	–	–	–
$Y_{0.1}Zr_{0.9}O_{1.95}$	40.729	119.8	0.0186	0.00252	0.0409
$Y_{0.2}Zr_{0.8}O_{1.90}$	40.385	120.7	0.0377	0.00472	0.0792
$Y_{0.3}Zr_{0.7}O_{1.85}$	40.041	121.5	0.0571	0.00663	0.1150
$Er_{0.1}Zr_{0.9}O_{1.95}$	43.341	119.7	0.1686	0.00269	0.1793
$Er_{0.2}Zr_{0.8}O_{1.90}$	45.609	120.6	0.2959	0.00508	0.3181

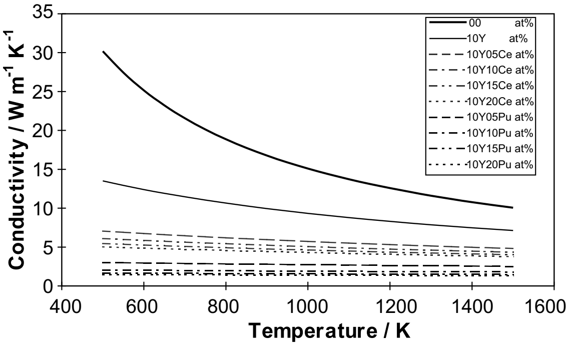

Fig. 2. Calculated intrinsic thermal conductivity of $Y_y(Ce/Pu)_zZr_{1-y-z}O_{2-y/2}$ as a function of temperature. Conditions: Debye temperature T_D 500 K and the Grüneisen constant γ 2.1.

4. New experimental results and discussion

The thermal conductivity is simply the product of the density ρ, the specific heat capacity C_V (intrinsic thermodynamic property, which can be estimated for ideal solid solution as $C_V = \sum x_i \cdot C_{Vi}$, with x_i the molar fraction of each components) and of the thermal diffusivity D, which is experimentally determined, for example, using the laser flash method.

$$\kappa = \rho \cdot C_V \cdot D. \tag{16}$$

The thermal diffusivity of the studied samples was measured as a function of the temperature. The samples $Er_{0.07}Y_{0.10}Ce_{0.15}Zr_{0.68}O_{1.913}$ (COP), $Er_{0.04}Y_{0.14}Pu_{0.09}Zr_{0.73}O_{1.91}$ (ATT) and $Er_{0.04}Y_{0.14}Pu_{0.08}Zr_{0.74}O_{1.91}$ (COP) were prepared as reported earlier [30], (COP) referring to a coprecipitation preparation and (ATT) to attrition milling production. The relative density was 0.900, 0.944 and 0.863 respectively and the grain size was order of 20 μm. The tests were carried out by laser flash as described by Parker et al. [31]. The 1 mm disk samples were coated with C or W and the tests performed with temperature ramp of 5–10 K min^{-1} and with measurements during heating and cooling. The inverse of the diffusivity of Pu–zirconia IMF followed a linear trend with temperature in the range 400–2000 K (see Fig. 3).

The thermal conductivity of the (Ce/Pu)–IMF samples of composition $Er_xY_yM_zZr_{1-x-y-z}O_{2-(x+y)/2}$ (with M = Ce or Pu, $z = 0$ or $\sim$0.1 and $x + y = 0.15$) lies between 2.7 and 1.7 W K^{-1} m^{-1} (see Fig. 4). Porosity, which has a pronounced effect on the sample thermal conductivity κ_η, was corrected using a simple correction $\kappa = \kappa_\eta(1-\eta)^{1.7}$ [32] and the bulk material conductivity κ is plotted as a function of temperature. These values are much smaller than for pure dense zirconia, as reported for the samples obtained by sintering nanophases [17]. This thermal conductivity is comparable to that of urania. The additions of yttria, erbia and plutonia required for the stabilisation of zirconia and the safety in-pile, have a tremendous degrading effect on the thermal conductivity of zirconia at low temperature. The effect is comparable to that observed by the addition

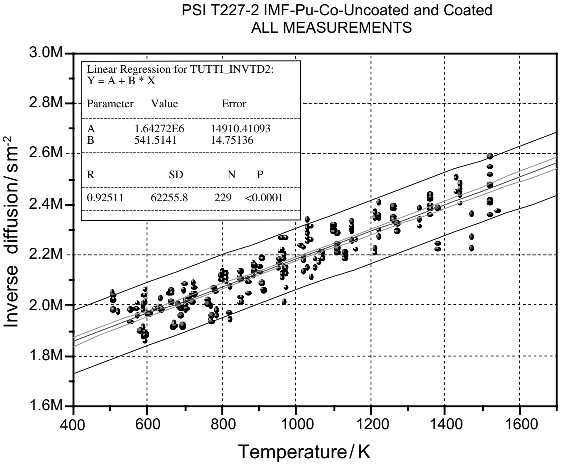

Fig. 3. Thermal diffusivity of $(Er,Y,Pu,Zr)O_{2-\xi}$ as a function of temperature. Conditions: laser flash, 1-mm thick disk of samples $Er_{0.04}Y_{0.14}Pu_{0.08}Zr_{0.74}O_{1.91}$ (COP), coated with C or W or uncoated, temperature ramp 5–10 K min^{-1} with measurements during heating and cooling temperature program. M for 10^6.

Table 5
The scattering cross-sections and thermal resistivities ΔW due to CeO_2 or PuO_2 addition

Cubic zirconia	$\overline{M}$ (g mol^{-1})	$\bar{r}$ (pm)	$\Delta\Gamma_M$	$\Delta\Gamma_r$	ΔW (m K W^{-1})
$Y_{0.1}Zr_{0.9}O_{1.95}$	40.729	119.8	–	–	–
$Y_{0.1}Ce_{0.05}Zr_{0.85}O_{1.95}$	41.544	120.0	0.0407	−0.00110	0.0267
$Y_{0.1}Ce_{0.10}Zr_{0.80}O_{1.95}$	42.359	120.2	0.0770	−0.00220	0.0494
$Y_{0.1}Ce_{0.15}Zr_{0.75}O_{1.95}$	43.174	120.5	0.1093	−0.00329	0.0684
$Y_{0.1}Ce_{0.20}Zr_{0.70}O_{1.95}$	43.989	120.7	0.1380	−0.00439	0.0841
$Y_{0.1}Pu_{0.05}Zr_{0.85}O_{1.95}$	43.242	120.0	0.2488	−0.00103	0.2170
$Y_{0.1}Pu_{0.10}Zr_{0.80}O_{1.95}$	45.755	120.2	0.4337	−0.00206	0.3760
$Y_{0.1}Pu_{0.15}Zr_{0.75}O_{1.95}$	48.268	120.4	0.5703	−0.00309	0.4910
$Y_{0.1}Pu_{0.20}Zr_{0.70}O_{1.95}$	50.781	120.6	0.6697	−0.00411	0.5720

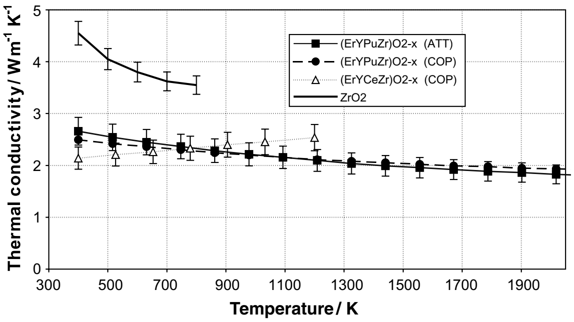

Fig. 4. Comparison of bulk thermal conductivities for ZrO_2 and $Er_xY_y(Ce/Pu)_zZr_{1-x-y-z}O_{2-(x+y)/2}$ as a function of temperature. Conditions: Data for ZrO_2 from [17]; the relative density of samples $Er_{0.07}Y_{0.10}Ce_{0.15}Zr_{0.68}O_{1.913}$ (COP), $Er_{0.04}Y_{0.14}Pu_{0.09}Zr_{0.73}O_{1.91}$ (ATT) $Er_{0.04}Y_{0.14}Pu_{0.08}Zr_{0.74}O_{1.91}$ (COP) are 0.900, 0.944 and 0.863 respectively and the thermal conductivity was corrected for the porosity.

of gadolinia to urania e.g. Hirai and Ishimoto [33] or by doping urania with various tetra- or tri-valent oxides e.g. Lemehov et al. [34]. These samples are gray due to Pu(IV) presence and its potential of light absorption favoring energy transfer by phononic processes. $Er_{0.05}Y_{0.10}Ce_{0.10}Zr_{0.75}O_{1.925}$ is white, slightly yellow, and does not absorb significantly light compared to the Pu doped sample. This enables energy transfer by radiance to play a role. This must be treated separately as a non-intrinsic property. However, photonic conductivity does not follow a κ_{pht}/T^3a^{-1} law [35] because the absorption a is variable in the near-infrared. These IMF samples have conductivities rather temperature invariant of about 2 W m^{-1} K^{-1}. If this experimental result cannot be formally calculated (see Gibby [8]), it can be understood using Eq. (1): for pure zirconia, the term $B \cdot T$ is predominant and the conductivity follows an hyperbolic trend with temperature, while, when Y, Er and Pu/Ce are added as dopant the extrinsic term A increases and the thermal conductivity plot passes from the hyperbolic form to a flat relationship. This was recently confirmed by Wu et al. [37] for the ZrO_2–$GdO_{1.5}$ system, for which conductivity is calculated in a semi-empirical way. The only way to increase the conductivity would be to decrease the dopants (Y and Er) fraction.

5. Summary and concluding remarks

The study of the thermal conductivity of cubic stabilized zirconia IMF of formula

$$Er_xY_yM_zZr_{1-x-y-z}O_{2-(x+y)/2}$$

(with M = Ce or Pu, $z = 0$ or $\sim$0.1 and $x + y \sim 0.15$), has been achieved. The limited number of data for these quaternary zirconia's justifies this formal and experimental study. Both approaches (Klemens model and that applied by Gibby) were revisited, compared and found to result similar feature. The derived conductivity models were applied for zirconia, accounting the effects of isotopes, impurities and dopants. The model may be only used in a semi-quantitative way and adjusting corrections are needed.

It is experimentally observed that the thermal conductivity is rather constant as a function of temperature in the range 400–2000 K. This behaviour is justified theoretically and verified semi-quantatively when applying the model. The thermal conductivity was observed to depend on the concentration of dopants such as $YO_{1.5}$ and/or $ErO_{1.5}$, CeO_2 (analogous of PuO_2) or PuO_2. In the lattice of zirconia, isotopes, impurities, dopants and oxygen vacancies act as phononic scattering centers contributing to conductivity reduction with regard to pure zirconia. The experimental conductivity of the $Er_{0.05}Y_{0.10}Pu_{0.10}Zr_{0.75}O_{1.925}$ materials is about 2 W m^{-1} K^{-1}. The thermal conductivity of stabilized cubic zirconia based IMF may be improved by using a minimum of trivalent dopants (Er, Y), which is Pu loading connected and may be by producing material with large grains and very low porosity.

Since the thermal conductivity of a zirconia based IMF is rather low, other fuel designs such as hollow pellet may be suggested for optimal utilisation of the fissile material in light water reactor. The solid solution IMF may be utilised as hollow pellet. Similar calculations may be performed for other actinide doping in zirconia, and for the utilisation of target for minor actinide incineration.

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. Acknowledgements are due to Drs F. Ingold and M. Pouchon for their interest and discussions of this work. The plutonia doped samples produced at the Paul Scherrer Institute were 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. Acknowledgements are also due to Dr R. Mévrel from ONERA, Paris for his constructive review of the manuscript.

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