

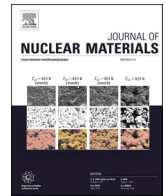


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Thermal conductivity analysis of UO₂-based fuel by relaxation-time approximation method

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HIGHLIGHTS

- The thermal conductivities of single-crystalline UO₂, polycrystalline UO₂, and polycrystalline UO₂ solid solutions were measured and analyzed using the relaxation-time approximation method.
- The determined phonon scattering parameters successfully reproduced the thermal conductivities of the fabricated samples and accurately represented previously reported data for MA-containing UO₂.

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ABSTRACT

The effects of solute elements and oxygen vacancies on the thermal conductivity of UO₂ were quantitatively evaluated using the relaxation-time approximation method. In UO₂ fuel, all solute elements—including various FP, burnable poisons such as Gd, Pu in MOX fuel, and added MA—reduce the thermal conductivity. The magnitude of this reduction depends on the specific element and the effects overlap, making quantitative evaluation challenging. In this study, these effects were analyzed using the relaxation-time approximation method by determining the relevant phonon scattering parameters.

Single-crystalline and polycrystalline UO₂ samples, as well as polycrystalline UO₂ solid solutions, were fabricated, and their thermal conductivities were measured. The thermal conductivity was found to decrease with increasing differences in atomic mass and ionic radius between the solute elements and uranium ions, as well as with increasing oxygen vacancy concentration. Based on these results, phonon scattering parameters, including the Grüneisen constant, were determined. The determined parameters successfully reproduced the thermal conductivities of the fabricated samples and accurately represented previously reported data for MA-containing UO₂. These parameters can therefore be used to predict the thermal conductivity of a wide range of UO₂-based fuels.

1. Introduction

The thermal conductivity of nuclear fuels governs fuel temperature and indirectly affects fuel properties such as creep behavior and fission gas release rates. UO₂ is widely used as fuel in light water reactors and is therefore one of the most extensively studied materials with respect to thermal conductivity [1–7]. UO₂ has a cubic fluorite-type structure that remains stable over the entire temperature range up to its melting point and can accommodate a variety of cationic solute elements, as well as

oxygen defects within its lattice.

The thermal conductivity of UO₂ fuel is influenced by various factors, including soluble FP elements, FP precipitates, grain size, porosity, and oxygen defects. A diverse range of FPs is produced and accumulates during reactor operation, and the concentration of oxygen defects varies depending on the atmosphere within the fuel rods. In UO₂, oxygen defects exist as oxygen vacancies and interstitial oxygen (Frenkel pairs), and it is known that they form clusters, particularly at high temperatures [8]. Additionally, certain solute elements are often added to UO₂

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initially, such as Gd as a burnable poison, Pu in MOX fuel, and MA for transmutation. Such changes in the initial composition affect both the species and the quantity of generated FPs. These effects on thermal conductivity overlap, making it difficult to evaluate them individually and to estimate the thermal conductivity of irradiated UO₂ fuel. For this reason, simplified equations based on experimental results for irradiated or simulated fuels are generally employed, using burnup and other variables as limited parameters. As an example, the following Eq. (1-1) is used [5,9–13].

$$\kappa = \frac{1}{A + BT} \quad (1-1)$$

where κ denotes the thermal conductivity, T is the absolute temperature, A is a constant that includes all temperature-independent effects, such as point defect scattering and grain boundary scattering of phonons, and B is a constant that represents phonon–phonon scattering. Although this equation reproduces experimental values well, it is overly simplified and does not permit a quantitative evaluation of individual phonon scattering. The parameters A and B determined for pure UO₂ fuel cannot be directly applied to other UO₂-based fuels, such as MOX fuel and MA-containing fuel. In recent years, various UO₂ fuels for innovative reactors have been considered, and fuel property data, including thermal conductivity, are required for their practical implementation. However, fuel fabrication, irradiation testing, and property measurements require significant cost and effort. Therefore, a fuel property evaluation method applicable to a wide range of UO₂-based fuels is desired.

In UO₂, phonons are the dominant heat carriers at least up to approximately 2000 K. Phonons are quantized lattice vibrations that are scattered by point defects and grain boundaries and are useful for describing heat transport phenomena. Heat conduction can be described by specifying the phonon sound velocity and the relaxation time associated with each scattering mechanism. This approach is known as the relaxation-time approximation method [14]. In this method, the thermal conductivity, κ , due to phonon transport is given by the following Eq. (1-2).

$$\kappa = \int_0^{\omega_{\max}} C_{ph} \cdot v \cdot \Lambda d\omega = \int_0^{\omega_{\max}} C_{ph} \cdot v^2 \cdot \tau d\omega \quad (1-2)$$

where C_{ph} denotes the phonon specific heat, v is the phonon group velocity, Λ is the mean free path, ω is the phonon frequency, and τ is the phonon relaxation time. The relaxation time can be obtained by applying Matthiessen's rule, as shown in Eq. (1-3), to the relaxation times associated with each scattering.

$$\Lambda = v \cdot \tau,$$

$$\frac{1}{\tau} = \frac{1}{\tau_U} + \frac{1}{\tau_{spin}} + \frac{1}{\tau_{GB}} + \frac{1}{\tau_{def}} + \dots \quad (1-3)$$

where τ_U is the relaxation time for phonon–phonon scattering, τ_{spin} is that for phonon–spin scattering, τ_{GB} is that for phonon–grain boundary scattering, and τ_{def} is that for phonon–point defect scattering. As mentioned above, the composition of nuclear fuel changes during irradiation, and a variety of initial compositions also exist. The relaxation-time approximation approach, which can be applied to a wide range of fuel compositions, is therefore useful for analyzing the thermal conductivity of nuclear fuels.

In this study, the thermal conductivity of UO₂ and its solid solutions is analyzed using the relaxation-time approximation method. The thermal conductivities of single-crystalline UO₂ and polycrystalline UO₂ samples containing various solute elements or oxygen vacancies were measured, and the phonon-scattering parameters for each scattering process were determined based on the experimental thermal conductivity data. The obtained parameters can be used universally for evaluating the thermal conductivity of UO₂ and can be applied to a variety of

UO₂-based fuels.

2. Relaxation-time approximation method

In the thermal conductivity expression given by Eq. (1-2), $\omega_{\max}$ is the maximum phonon frequency assumed. To obtain the phonon specific heat and group velocity, the sine function [15,16] shown in Eq. (2-1) is used in this study for the ω - k dispersion relation.

$$\omega = \omega_0 \sin\left(\frac{\pi}{2} \frac{k}{k_0}\right) \quad (2-1)$$

where ω_0 , k_0 are scaling parameters determined for each substance. Dames et al. showed that ω_0 and k_0 can be derived from the sound velocity v_s and the atomic density N of the substance as shown in Eq. (2-2) [16].

$$k_0 = (6\pi^2 N)^{1/3}, \quad \omega_0 = \frac{2}{\pi} v_s (6\pi^2 N)^{1/3} \quad (2-2)$$

The specific heat given by the equations corresponds to harmonic lattice vibrations. It does not account for the thermal expansion term, nor does it account for the increase due to Frenkel pair formation, which is observed in UO₂ at high temperatures. It should be noted that this approximation is applicable only to temperature ranges where such increases in specific heat and heat conduction due to small polarons do not occur.

Then, we discuss the relaxation time for each phonon scattering process.

2.1. Phonon–phonon scattering

Phonon–phonon scattering can be classified into normal processes, in which momentum is conserved before and after scattering, and Umklapp scattering, in which momentum is not conserved. In this study, the influence of normal processes is assumed to be small and is therefore neglected. Various expressions have been proposed for the relaxation time associated with Umklapp scattering [14,17–19], and in this study, Eq. (2-3) proposed by Morelli [19] is employed.

$$\frac{1}{\tau_U} = \frac{\hbar \gamma^2}{M v^2 \theta} \omega^2 \text{Exp}\left(-\frac{\theta}{3T}\right) \quad (2-3)$$

where T is the temperature, θ is the Debye temperature, M is the mean atomic weight, $\hbar = 2\pi\hbar$ is Planck's constant, v is the sound velocity, and γ is the Grüneisen constant. If the sound velocity and average atomic weight of the sample are known, the only unknown parameter is γ , which can be used to determine the relaxation time for Umklapp scattering.

2.2. Phonon–spin scattering

Based on thermal conductivity measurements of single-crystalline UO₂ at very low temperatures, Gofryk et al. reported the existence of phonon-spin scattering [20]. The thermal conductivity of UO₂ exhibits a sharp change near the Néel temperature, which is interpreted as a transition from the antiferromagnetic to the paramagnetic phase. This transition results in a random orientation of U-ion spins and the scattering of phonons with a certain frequency. By taking this frequency as the resonance frequency $\omega_{s,i}$, the relaxation time, τ_{spin} , for phonon–spin scattering can be expressed by the following Eq. (2-4).

$$\frac{1}{\tau_{spin}} = \sum_i \frac{C_i \omega^4}{(\omega^2 - \omega_{s,i}^2)^2} F_i(T) \quad (2-4)$$

where C_i is the coupling constant and $F_i(T)$ is the excitation fraction of energy level i , which can be expressed by the following Eq. (2-5) [21]

$$F_i(T) = \frac{1 - \exp\left(-\frac{\hbar\omega_{s,i}}{k_B T}\right)}{1 + \exp\left(-\frac{\hbar\omega_{s,i}}{k_B T}\right)} \quad (2-5)$$

This equation indicates that as the phonon frequency approaches the resonance frequency, it becomes a strong scattering source and the relaxation time becomes very short. The resonance frequencies $\omega_{s,1}$ and $\omega_{s,2}$ have been reported as 5.8×10^{12} Hz and 5.9×10^{12} Hz, respectively [21]. In this study, the relaxation time for phonon–spin scattering is determined by treating the coupling constants C_i as fitting parameters.

2.3. Phonon–grain boundary scattering

Several models for phonon–grain boundary scattering have been proposed. One is the simple Gray model, which assumes that phonons are always scattered at grain boundaries. In this study, we use the Non-gray model proposed by Wang [15], in which the scattering depends on the phonon frequency (Eq. (2-6)).

$$\frac{1}{\tau_{GB}} = \frac{v_s}{\alpha l_{GB} \beta \cdot \frac{\omega_0}{\omega}} \quad (2-6)$$

where l_{GB} is the average grain size, and α is the parameter for grain boundary transmission, with 0.72 being the recommended value. The value of β is calculated to be 0.7. The Non-gray model is adopted in this study because it accounts for the dependence of grain boundary transmittance on phonon frequency.

2.4. Phonon–point defect scattering

Phonons are scattered by point defects, that is, lattice imperfections. The following Eq. (2-7) formalizes the scattering caused by elemental substitution, a type of lattice defect, and shows that the scattering strength depends on the differences in atomic weight and ionic radius between the substituting element and the host element [22–24].

$$\frac{1}{\tau_{def}} = A\omega^4 = \frac{V\omega^4}{4\pi v^3} \Gamma, \quad \Gamma = \sum_i x_i \left\{ \left(\frac{\Delta M}{M} \right)^2 + \epsilon \left(\frac{\Delta r}{r} \right)^2 \right\} \quad (2-7)$$

where V is the volume per atom, x_i is the fraction of atom i , M is the mean atomic mass, r is the mean atomic radius, and ΔM and Δr are the mass difference and ionic radius difference between the substituting and host atoms, respectively. The parameter ϵ governs the scattering due to the ionic radius difference and is often treated as a fitting parameter. As the atomic masses and ionic radii of oxide materials are well known [25], the only unknown is ϵ . In other words, if ϵ is determined through analysis, the effect of elemental substitution can be quantitatively evaluated.

Next, we consider the effect of oxygen defects. Oxygen defects include oxygen vacancies, interstitial oxygen atoms, and clusters. Considering the sample composition, the temperature range, and the atmosphere, this study considers only oxygen vacancies. Charge compensation due to oxygen vacancies is achieved through changes in the valence of cations. As oxygen vacancies occur at anion sites, a different value of ϵ should be used. In addition, the mass and ionic radius difference for oxygen vacancies is difficult to define. Therefore, in Eq. (2-8), point defect scattering due to oxygen vacancies is expressed by introducing the vacancy concentration δ and combining the contributions from mass and ionic radius differences.

$$\Gamma = \delta \Gamma_O \quad (2-8)$$

where Γ_O is a parameter used to evaluate the effect of oxygen vacancies,

which is determined through analysis.

In this study, the parameters necessary for the above relaxation times were determined by fitting to measured thermal conductivity data. The phonon–phonon, spin, and grain boundary scattering parameters were obtained from data for single- and polycrystalline UO_2 . The point defect scattering parameter ϵ was determined from measurements of Zr or Th dissolved UO_2 samples without oxygen vacancies, and the oxygen vacancy parameter Γ_O was determined from results for $\text{U}_{1-x}\text{M}_x\text{O}_{2-\delta}$ (M: trivalent solute elements) samples.

3. Experimental methods

3.1. Sample preparation

To determine the relaxation times, single crystalline UO_2 , polycrystalline UO_2 , $\text{U}_{1-x}\text{M}_x\text{O}_{2-\delta}$ (M=Th, Zr, Y, Gd, Er; $x=0.02, 0.05$), and $\text{U}_{1-x}\text{M}_x\text{O}_{2-\delta}$ (M=Nd; $x=0.02, 0.05, 0.10, 0.20, 0.50$) were evaluated. The single-crystalline UO_2 sample was a (100) oriented rectangular specimen with a thickness of 1 mm. For the polycrystalline samples, in addition to UO_2 and ThO_2 powders, ZrO_2 (Fruuchi Chemical, 99.9%) and M_2O_3 (M=Y, Nd, Gd, Er, Kojundo Kagaku, 99.9%) powders were used as starting materials. Prior to weighing, the UO_2 powder was heat-treated in a 4% H_2 -Ar atmosphere at 873 K for 2 h to obtain an O/U ratio of 2.0. Other oxide powders were oxidized to M_2O_3 or MO_2 in an electric furnace at 1073 K for 2 h in air. Then these powders were weighed to stoichiometric ratios. The weighed powders were mixed using an agate mortar, cold-pressed into pellets, and subjected to a solid-state reaction at 1873 K for 72 h in a 4% H_2 -Ar atmosphere. After the reaction, the samples were manually ground and then finely granulated using wet ball milling. The resulting powder was packed into a graphite die and densified by spark plasma sintering in an Ar flow (SPS-515S, Sumitomo Coal Mining Co.). Sintering was performed at 1773 K for 10 min under an applied pressure of 50 MPa. To adjust the O/U ratio of the sintered samples, they were subsequently heat-treated in a 4% H_2 -Ar atmosphere at 1473 K for 5 h in an electric furnace.

3.2. Sample identification

The crystal structures of the prepared samples were characterized by X-ray diffraction using a Rigaku Ultima IV X-ray diffractometer with $\text{Cu-K}\alpha$ radiation, over a diffraction angle range of $2\theta = 20^\circ \sim 120^\circ$. The measured XRD patterns were externally corrected using Si standards to determine the lattice parameters. Sample density was calculated from the measured dimensions and mass, and the relative density was obtained based on the determined lattice constant. For polycrystalline UO_2 samples, grain morphology was additionally evaluated using EBSD measurements in conjunction with FE-SEM (JEOL, 6500F).

3.3. Sound velocity measurement

Longitudinal and transverse sound velocities of the prepared samples were measured using the sing-around method, with a UVM-2 longitudinal transducer of 5 MHz and a transverse transducer of 10 MHz. From the obtained longitudinal and transverse sound velocities, the average sound velocity v_m and the Debye temperature θ were determined using the following Eqs. (3-1) and (3-2), respectively.

$$v_m = \left\{ \frac{1}{3} \left(\frac{1}{v_L^3} + \frac{2}{v_S^3} \right) \right\}^{-1/3} \quad (3-1)$$

$$\theta = \frac{h}{k} \left(\frac{3q\rho N_A}{4\pi M} \right)^{1/3} \quad (3-2)$$

where v_L is the longitudinal sound velocity, v_S is the transverse sound velocity, and k is Boltzmann's constant. N_A is the Avogadro constant, and q is the number of atoms per unit volume.

3.4. Thermal conductivity measurement

Thermal diffusivity was measured using the laser flash method with a thermal constant analyzer (LFA457, NETZSCH) over the temperature range from room temperature to 1173 K. In this study, thermal diffusivity was evaluated using the half-time method, and the Cowan correction was applied to account for heat loss from the sample surface. Using the obtained thermal diffusivity α , specific heat C_p , and sample density ρ , the thermal conductivity κ was calculated using the following equation.

$$\kappa = \alpha C_p \rho \quad (3-3)$$

The specific heat capacity was estimated by summing the specific heats of UO_2 and the added oxides [26] according to Neumann–Kopp's law.

All of the produced materials exhibited high density, ranging from 94% to 99% of the theoretical density. To account for this porosity, the Maxwell–Eucken equation [27,28] was applied to correct the thermal conductivity to a value corresponding to 100% density.

$$\kappa_{100} = \kappa_p \frac{1 + \beta P}{1 - P} \quad (3-4)$$

where κ_{100} is the thermal conductivity at theoretical density, κ_p is the thermal conductivity at porosity P , and β is a constant that depends on the pore shape. In this study, $\beta = 0.5$ was used, which is appropriate for spherical pores. Other equations, such as Loeb equation, have been proposed for porosity correction [3]. However, this equation includes experimental parameters, and the range of compositions to which it applies is unclear. Since it has no unknown parameters, the Maxwell–Eucken equation was employed in this study.

4. Results and discussion

4.1. Sample identification

XRD patterns of single-crystalline (sc-) and polycrystalline (pc-) UO_2 , as well as $\text{U}_{1-x}\text{M}_x\text{O}_{2-\delta}$ ($x=0.05$) and $\text{U}_{1-x}\text{Nd}_x\text{O}_{2-\delta}$ ($x=0.02-0.5$), are shown in Fig. 1, together with the PDF for UO_2 . The peak of sc- UO_2 corresponds to the (100) reflection in the PDF, confirming the crystal orientation. No impurity peaks were observed in any of the XRD patterns. These results indicate that the additive elements are homogeneously dissolved and

that single-phase samples with a fluorite-type structure were successfully obtained. Since it was not detected by XRD measurement, even if impurity phases were present, they would be sufficiently small to have negligible effect on thermal conductivity.

Table 1 presents the lattice constants and relative densities obtained from these XRD patterns. All samples exhibit high densities, exceeding 94% of the theoretical density. The concentration of oxygen vacancy, δ , was calculated from the experimental data using the following reported Eq. (3-5) [29].

$$a = \frac{4}{\sqrt{3}} \{ (1 - y - x) \cdot r_{\text{U}^{4+}} + y \cdot r_{\text{U}^{5+}} + x \cdot r_{\text{M}^{3+}} + (1 - \delta) \cdot r_{\text{O}^{2-}} + \delta \cdot r_{\text{O}^{\text{vac}}} \} \quad (3-5)$$

where a is the experimentally measured lattice constant, r represents the ionic radii from Shannon [25], $r_{\text{O}^{\text{vac}}}$ is the effective size of the oxygen vacancy [29], x is the concentration of the added elements, and y is the amount of U^{5+} . Here, added Zr and Th are assumed to have a valence of +4, and the O/M ratio of the solid solution containing these elements is assumed to be 2.0. Furthermore, all the rare earth elements are assumed to have a valence of +3, and charge compensation is achieved through the formation of oxygen vacancies and U^{5+} ions. The amounts of these formed were determined to correspond to changes in the lattice constant [29].

The IPF map image obtained from EBSD observations of pc- UO_2 is shown in Fig. 2. The grain orientations are almost random, indicating that the influence of SPS on grain alignment is negligible. The average grain size, calculated from the area of individual grains, is approximately 10 μm .

4.2. Sound velocity measurements

Table 1 presents the longitudinal sound velocity values prior to correction for sample density. Within the range of elemental additions of $x=0.05$ or less, the effect on sound velocity was minimal, and the observed variations were primarily attributed to porosity. Therefore, the reported values of 5479 m s^{-1} for v_L , 2801 m s^{-1} for v_S , and 3138 m s^{-1} for v_m were adopted as the sound velocities of polycrystalline UO_2 at 100% density [30,31]. These values are in close agreement with the measured results. As described below, a decrease in sound velocity is observed in samples with high Nd concentration. Given that the melting point of Nd_2O_3 is approximately 2500 K, lower than that of UO_2 , this suggests that the atomic bonds are weakened by the addition of Nd.

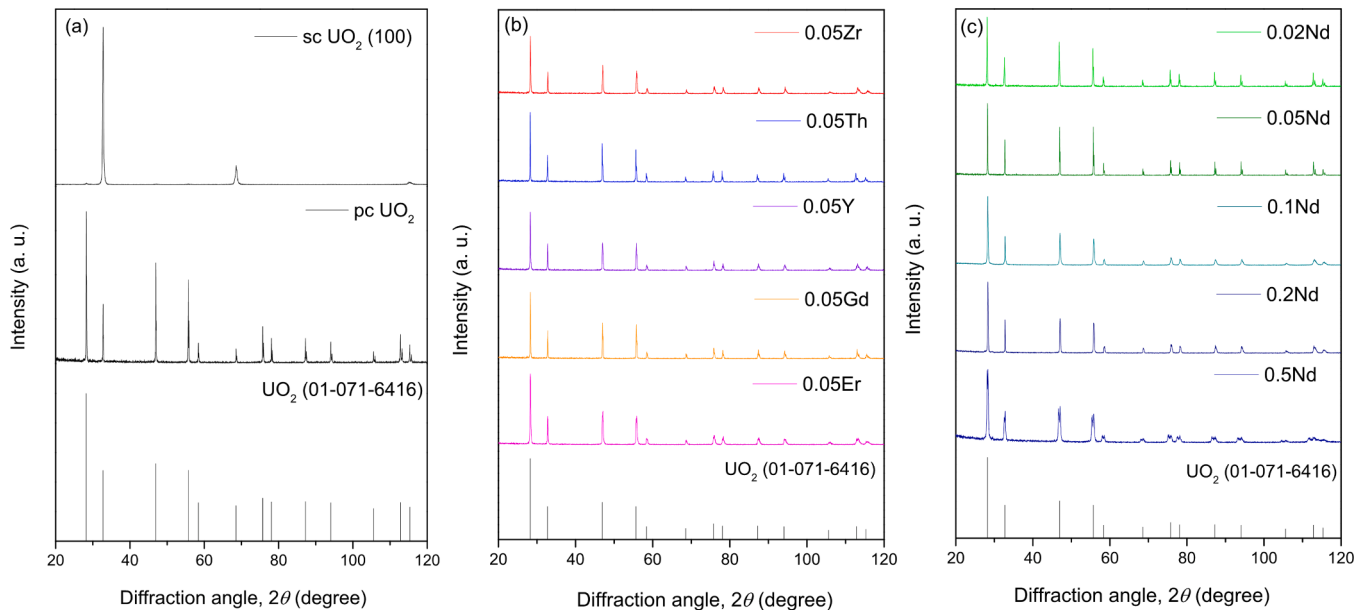


Fig. 1. XRD patterns of (a) sc- and pc- UO_2 , (b) $(\text{U}_{0.95}\text{M}_{0.05})\text{O}_{2-\delta}$ ($\text{M}=\text{Zr}, \text{Th}, \text{Y}, \text{Gd}, \text{Er}$), and (c) $\text{U}_{1-x}\text{Nd}_x\text{O}_{2-\delta}$ ($0.02 < x < 0.5$).

Table 1
Characteristics of the fabricated samples.

Added element	x in (U _{1-x} M _x)O _{2.6}	Notation in figures	Lattice constant a (nm)	O/M=2-δ	y, amount of U ⁵⁺	Relative density (%T.D.)	Longitudinal sound velocity* (m s ⁻¹)
-	0	sc UO ₂	-	2.000	0	-	-
	0	pc UO ₂	0.5471	2.000	0	96.22	5307
Zr	0.02	0.02Zr	0.5466	2.000	0	96.98	5380
	0.05	0.05Zr	0.5460	2.000	0	98.57	5450
Th	0.02	0.02Th	0.5472	2.000	0	96.54	5367
	0.05	0.05Th	0.5475	2.000	0	96.84	5391
Y	0.02	0.02Y	0.5468	1.995	0.0108	98.36	5390
	0.05	0.05Y	0.5459	1.998	0.0460	98.22	5473
Gd	0.02	0.02Nd	0.5467	1.995	0.0172	98.45	5463
	0.05	0.05Nd	0.5463	1.999	0.0455	99.12	5442
Er	0.02	0.02Er	0.5467	1.996	0.0122	97.45	5365
	0.05	0.05Er	0.5469	1.985	0.0250	98.21	5334
Nd	0.02	0.02Nd	0.5469	1.999	0.0175	97.38	5358
	0.05	0.05 Nd	0.5470	1.998	0.0446	99.23	5452
	0.1	0.1Nd	0.5467	1.999	0.0941	97.55	5059
	0.2	0.2Nd	0.5468	1.997	0.190	96.15	5253
	0.5	0.5Nd	0.5486	1.965	0.430	94.27	4902

sc: single crystalline, pc: polycrystalline

*before density correction

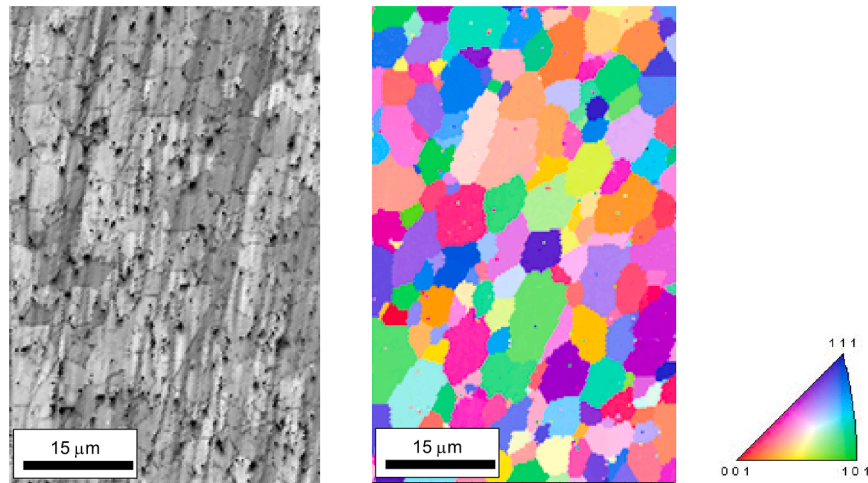


Fig. 2. EBSD image of polycrystalline UO₂ (2000x).

5. Thermal conductivity analysis

In this analysis, the following procedure was employed:

1. Using experimental data from sc- and pc-UO₂, the Grüneisen constant and C_i , which are the unknown parameters for the phonon–phonon and phonon–spin scattering terms, respectively, were determined. As discussed below, the effect of grain boundary scattering is small and therefore negligible.
2. Experimental data from (U,Zr)O₂ and (U,Th)O₂, containing tetravalent solute elements, were used to determine the unknown parameter ϵ for phonon–point defect scattering.
3. Experimental data from (U,M)O_{2.6} (M=Y, Gd, Er), containing trivalent solute elements and oxygen vacancies, were used to determine the oxygen vacancy parameter Γ_O .
4. For (U,Nd)O_{2.6} samples containing high Nd concentration, thermal conductivity was evaluated while accounting for the change in sound velocity.
5. For validation, all obtained phonon scattering parameters were applied to predict the thermal conductivity of MA containing UO₂.

5.1. Single/polycrystalline UO₂

The phonon scattering mechanisms in sc-UO₂ are phonon–phonon scattering (Umklapp scattering) and phonon–spin scattering, whereas pc-UO₂ additionally exhibits grain boundary scattering. The measured and analyzed thermal conductivities of sc- and pc-UO₂ are shown in Fig. 3, along with previously reported values [1–3,7,32–34]. The reported thermal conductivities of single-crystalline samples exhibit considerable variation, likely owing to the presence of small amounts of impurities or oxygen defects. The sc-UO₂ data from this study are close to those reported by Bates and are relatively high, indicating a low impurity content. The Grüneisen constant γ and C_i were obtained by fitting, yielding $\gamma = 1.6$ and $C_1 = C_2 = 0.11$. For the Grüneisen constant, the values are in good agreement with previously reported UO₂ values [35–37], supporting the validity of the analysis.

In pc-UO₂, the thermal conductivity values were nearly identical to those of sc-UO₂, as previously reported by Moore [2]. This indicates that the effect of grain boundary scattering is minimal for UO₂ with grain sizes of 10 μm or larger. Fig. 4 shows the thermal conductivity values at various temperatures, calculated using grain boundary scattering parameters $\alpha=0.72$ and $\beta=0.7$, which are the recommended values [15]. It is evident that the effect of grain boundary scattering is weak for grain sizes on the order of 10 μm, resulting in negligible changes in thermal

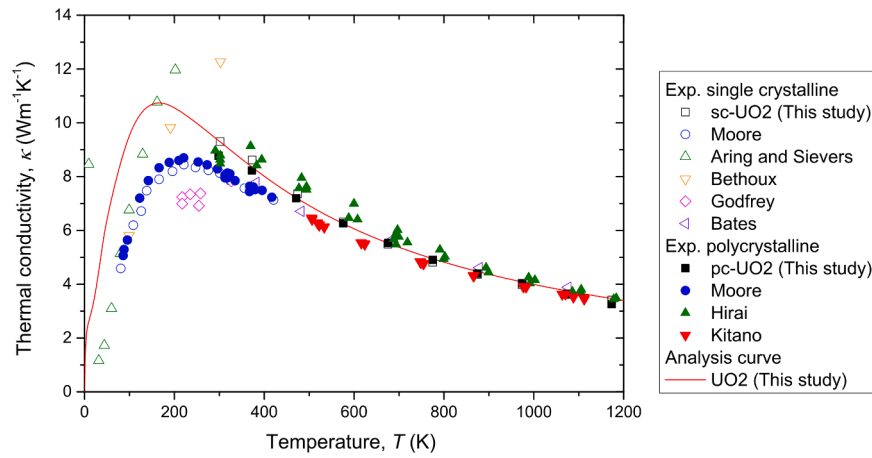
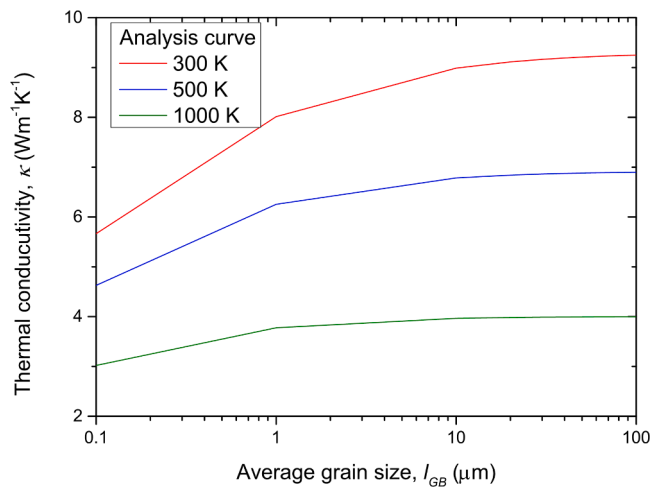
Fig. 3. Thermal conductivity of sc- and pc-UO₂.

Fig. 4. Grain-size dependence of thermal conductivity at 300 K, 500 K, and 1000 K.

conductivity. As UO₂ pellets used in conventional reactors typically have grain sizes of 10 μm or larger, the effect of grain boundary scattering can be considered almost negligible at least at temperatures equal to or higher than room temperature.

5.2. Tetravalent elements-containing UO₂

The phonon-point defect scattering parameters were then determined. Fig. 5 shows the thermal conductivity of UO₂ solid solutions containing Zr and Th, which are tetravalent elements like U. As Th⁴⁺ has only small differences in both atomic mass and ionic radius compared to U⁴⁺, the thermal conductivity is not significantly different from that of UO₂, as predicted by Eq. (2-6). In contrast, the thermal conductivity of the Zr-dissolved sample is markedly reduced owing to the larger differences in both atomic mass and ionic radius. By fitting the experimental data, the phonon-point defect scattering parameter was determined to be $\epsilon = 15$. The thermal conductivity curves obtained from this fitting are shown in Fig. 5, demonstrating good agreement with the experimental data. Using this parameter, the effect of solute elements with any atomic mass and ionic radius can be quantitatively evaluated.

The phonon frequencies most strongly affected by scattering depend on the specific scattering mechanism. Fig. 6 shows the mean free path, $l = v\tau$, for phonon-phonon scattering, phonon-spin scattering, grain boundary scattering, and point defect scattering when each occurs independently. Grain boundary scattering is constant across all phonon

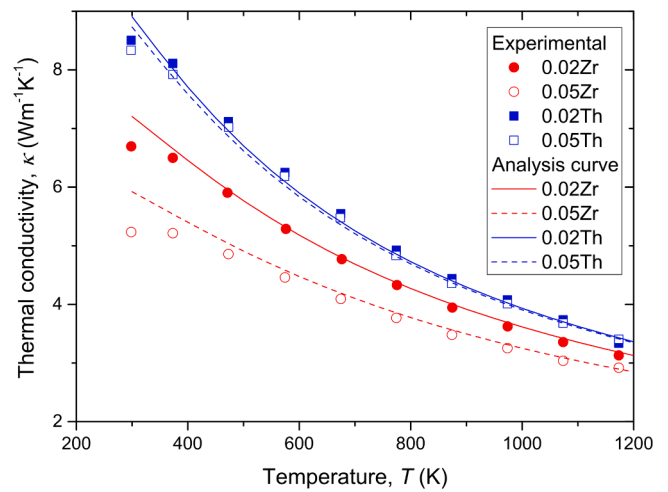
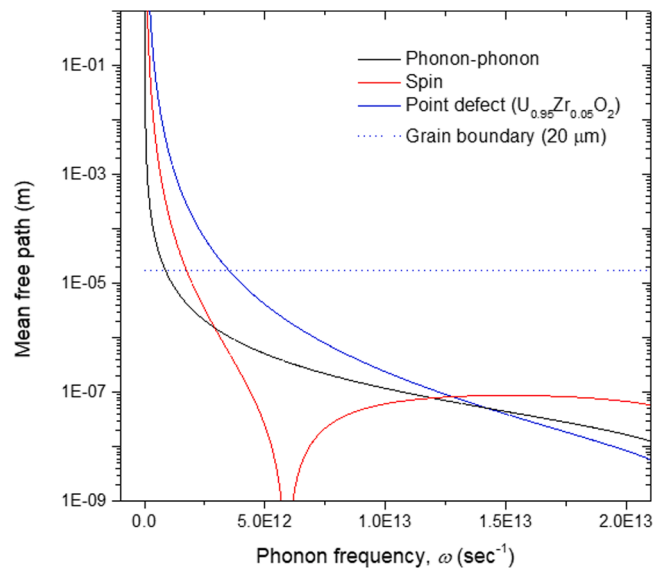
Fig. 5. Thermal conductivity of (U,Zr/Th)O₂ with fitted curves.

Fig. 6. Comparison of the mean free paths for each phonon scattering mechanism.

frequencies. In most frequency ranges, its mean free path exceeds that of

phonon–phonon scattering, indicating that grain boundary scattering is not a dominant scattering mechanism. In contrast, point defect scattering has a stronger effect on high-frequency phonons than phonon–phonon scattering. On the other hand, phonon–spin scattering strongly affects phonons near the resonance frequency of 5×10^{12} Hz, and its influence extends over a broad frequency range from 10^{12} to 10^{13} Hz. Therefore, even in single-crystalline UO_2 , the thermal conductivity is significantly lower than that of ThO_2 , as previously reported [20].

5.3. Oxygen vacancy term

We next discuss the thermal conductivity of UO_2 containing trivalent solute elements, which produce U^{5+} and oxygen vacancies for charge compensation. The concentrations of U^{5+} and the oxygen vacancy δ were calculated from the lattice constants, as shown in Table 1. The thermal conductivities of UO_2 solutions with Y, Gd, and Er are presented in Fig. 7. By fitting the experimental results, the scattering parameter Γ_O , representing the effect of oxygen vacancies, was determined to be 1.25. The fitted curve reproduces the experimental values well.

5.4. High concentration of solute element

The phonon scattering parameters were successfully determined for each scattering mechanism in samples with elemental additions of $x=0.05$ or less. During reactor operation, the amounts of FP produced are less than a few percent, even at high burnup, so their effect can be evaluated using the above scattering parameters. However, new fuels may contain higher concentrations of solute elements such as Gd, Th, Pu, and MA. Therefore, we evaluated the thermal conductivity of samples with high Nd concentrations, as shown in Fig. 8, together with the fitted curve obtained using the previously determined scattering parameters. In the temperature range up to 800 K, the fitted curves are in good agreement with the experimental data for Nd concentrations of approximately $x<0.1$. However, for $x>0.2$, the fitted curves overestimate the experimental values, and the discrepancy increases with increasing Nd content. In this high-concentration region, changes in sound velocity can no longer be neglected. The dependence of the density-corrected sound velocity on Nd concentration is shown in Fig. 9, where the sound velocity decreases with increasing Nd content, reaching a reduction of approximately 10% at $x=0.5$. For this reason, the analysis was performed without modifying the phonon scattering parameters, while accounting only for the change in sound velocity. The results are shown in Fig. 10. After correcting for the change in sound velocity, the analytical results show reasonable agreement with the experimental data. For solid solutions with high solute concentrations ($x>0.1$), correction for changes in sound velocity is therefore considered necessary. It is also noted that the experimental thermal conductivity tends to exceed the analytical curve above approximately 800 K; however, the origin of this behavior remains unclear. One possibility is that, since

these samples contain a large number of oxygen vacancies, the formation of oxygen clusters may have played a role.

5.5. Validation of scattering parameters

To validate the determined scattering parameters, they were applied to previously reported thermal conductivity data for MA-containing UO_2 fuel, specifically $\text{U}_{0.68}\text{Pu}_{0.30}\text{Am}_{0.02}\text{O}_{2-\delta}$ reported by Morimoto [38]. These data are shown in Fig. 11, along with the analytical results obtained in this study. Considering the ionisation tendencies of each element, this analysis first assumes that all Am becomes trivalent, followed by Pu becoming trivalent until charge compensation is achieved. Good agreement between the analytical predictions and experimental values is observed for samples containing multiple solute elements and oxygen vacancies.

Using the scattering parameters obtained in this study, the thermal conductivity of UO_2 containing various elements, such as MA and FP, as well as oxygen vacancies, can be quantitatively evaluated. This approach enables the prediction of thermal conductivity for a wide range of UO_2 -based candidate fuels.

6. Conclusion

The thermal conductivities of single-crystalline UO_2 , polycrystalline UO_2 , and polycrystalline UO_2 solid solutions were measured and analyzed using the relaxation-time approximation method to determine the phonon scattering parameters. A summary of the obtained scattering parameters is presented in Table 2. Using these parameters, the thermal conductivity of UO_2 containing small amounts of any solute element and oxygen vacancies can be predicted. For higher solute concentrations, it is necessary to account for changes in the sound velocity.

It must be noted that the thermal conductivity values measured in this study and the parameters obtained from the analysis all carry uncertainty. Furthermore, interstitial oxygen, oxygen defect clusters, and small polaron conduction were not addressed in this study. Different approaches are required for analyzing the thermal conductivity of UO_2 with hyper-stoichiometric compositions or at high temperatures where cluster formation becomes prominent.

CRediT authorship contribution statement

Hiroaki Muta: Writing – review & editing, Writing – original draft, Project administration, Investigation, Formal analysis, Data curation, Conceptualization. **Naoki Kato:** Methodology, Investigation, Data curation. **Yuji Ohishi:** Supervision, Software, Formal analysis. **Yifan Sun:** Software, Formal analysis. **Kosuke Tanaka:** Supervision, Funding acquisition. **Koji Kitano:** Supervision, Formal analysis.

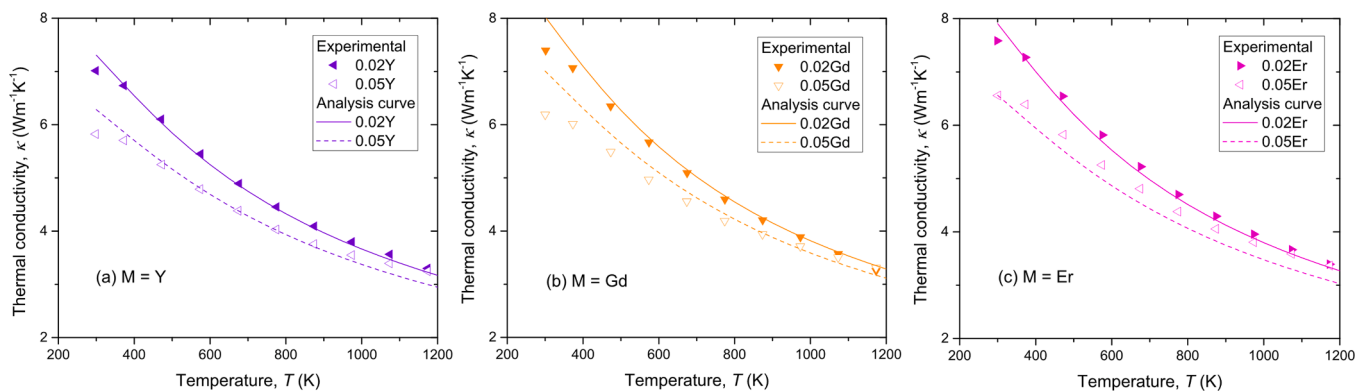


Fig. 7. Thermal conductivity of UO_2 solid solutions with oxygen vacancies: (a) $\text{U}_{1-x}\text{Y}_x\text{O}_{2-\delta}$, (b) $\text{U}_{1-x}\text{Gd}_x\text{O}_{2-\delta}$, and (c) $\text{U}_{1-x}\text{Er}_x\text{O}_{2-\delta}$ ($x = 0.02, 0.05$).

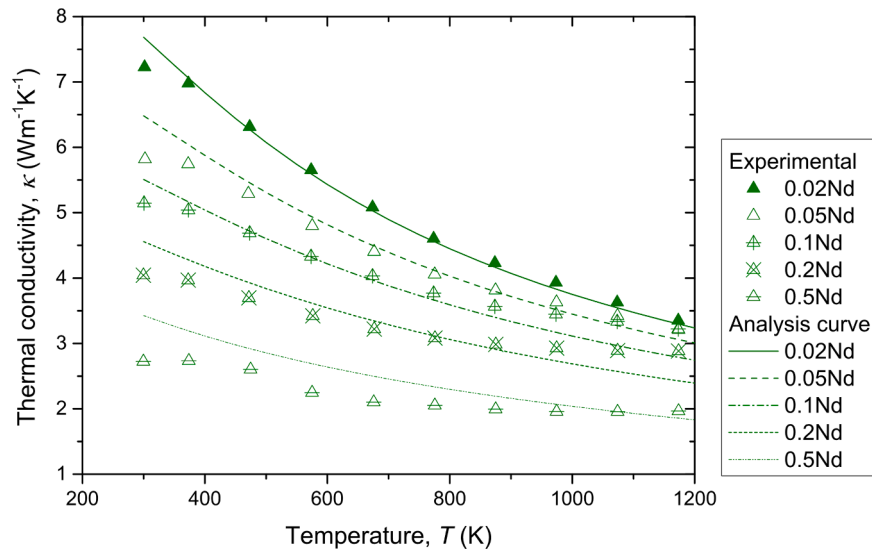
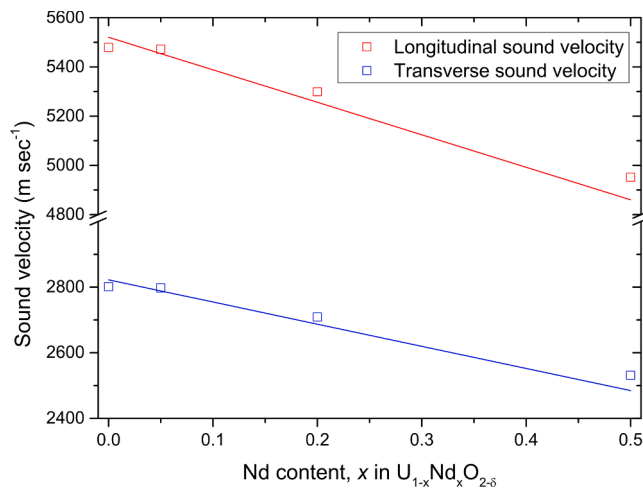
Fig. 8. Thermal conductivity of (U,Nd)O_{2-δ}.

Fig. 9. Dependence of sound velocity on Nd concentration, corrected for sample density [30].

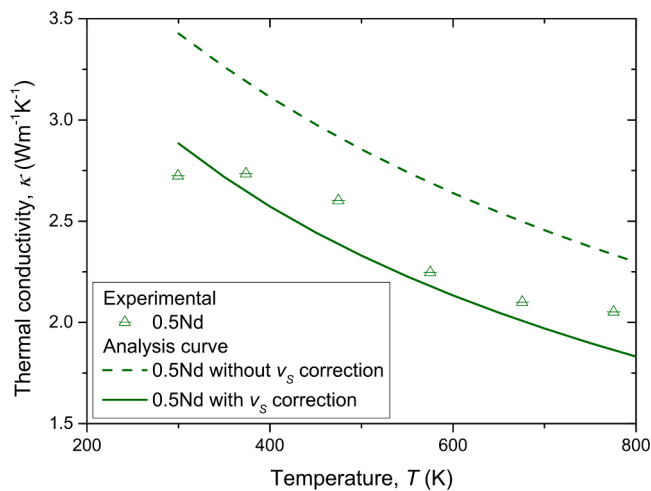


Fig. 10. Thermal conductivity analysis accounting for changes in sound velocity.

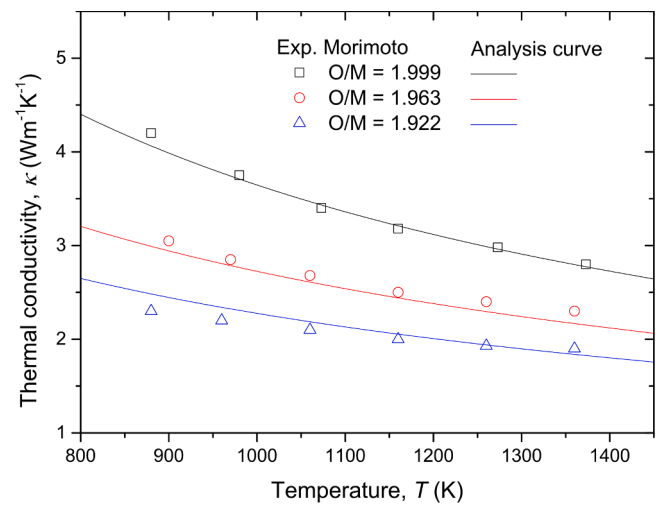
Fig. 11. Thermal conductivity analysis of MA-containing UO₂, U_{0.68}Pu_{0.30}Am_{0.02}O_{2-δ}.

Table 2

Phonon scattering parameters determined in this study.

Phonon scattering source	Parameter	Value	Unit
Phonon (Umklapp scattering)	γ	1.6	-
Spin	C_1	0.11×10^{12}	s ⁻¹
	C_2	0.11×10^{12}	s ⁻¹
Point defect	ϵ	15	-
Oxygen defect (point defect)	Γ_O	1.25	-

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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