Measurement of Thermal Properties of Nuclear Materials by Laser Flash Method

Yoichi TAKAHASHI & Masayuki MURABAYASHI

REVIEW

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The present status and prospects of the laser flash method for the measurement of thermal properties of nuclear materials are reviewed. Special emphasis is placed on the progress seen in experimental techniques for obtaining precise data on heat capacity and thermal diffusivity from 80 to 1,000 K. In this temperature range, the heat capacity and the thermal diffusivity of ceramic nuclear materials can be determined within a precision of $\pm 2\%$.

The data on heat capacity and thermal conductivity determined by the laser flash method are presented and discussed in respect of such nuclear materials as UO_2, U_4O_9, ThO_2, BeO, ThO_2-UO_2, ThO_2-CeO_2, UO_2-ZrO_2, ThO_2-BeO, UC, UN, US, UP, $UC_{1-x}N_x$ and $UP_{1-x}S_x$.

I. INTRODUCTION

The flash method for measuring the thermal properties of solid materials was first proposed by Parker et al.[1] in 1961. They measured the thermal diffusivity of metals by the use of a xenon flash lamp. Later on, Deem & Wood[2] utilized a ruby laser instead of flash lamp and demonstrated its suitability as enery source.

Moser & Kruger were the first to utilize the laser flash method for the determination of the thermal properties of nuclear materials. They reported the results of measurements on uranium compounds[3] and on plutonium compounds[4], for which they determined both the heat capacity and the thermal diffusivity from 300 to 900 K. Since then, the laser flash method has come to be recognized as useful for measurements of the high-temperature thermal properties of ceramic nuclear materials, as this method has many advantages

such as:
(1) short time required for measurement;
(2) relatively small effect of heat loss from the sample;
(3) small sample size required.

One of the promising characteristics of the laser flash method is that it permits measurements of thermal diffusivity to be extended up to very high temperatures such as 3,000 K by using infrared detectors for temperature measurement. Many experimental studies have been reported on the thermal diffusivity of ceramics, including important nuclear materials such as UO_2, at temperature above 1,000 K. These reports have recently been reviewed by Righini & Cezairliyan[5]. However, at high temperatures the accuracy of the temperature measurement is inevitably impaired because of the increasing heat exchange caused by radiation, thus by this method it becomes almost impossible to de-

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termine the heat capacity of samples at these temperatures.

On the other hand, it has been proved that the laser flash method can afford precise results of both heat capacity and thermal diffusivity at temperatures between 300 and 1,000 K. In particular the heat capacity measurement in this temperature range by the laser flash method gives rather more precise results[6] than those obtained by the usual adiabatic method.

This article covers the present status and prospects of the laser flash method for the measurement of thermal properties of nuclear materials. Particular reference will be made to the contribution made during the past several years by the present authors toward improvement of experimental techniques with a view to enhancing the accuracy of data obtained below 1,000 K. A brief summary will also be presented on the thermal properties of some nuclear materials, as determined by this method in the authors' laboratory.

II. DEVELOPMENTS IN EXPERIMENTAL TECHNIQUE

1. Principles of Laser Flash Method

The principles and experimental procedures adopted in the measurements of thermal diffusivity and heat capacity by means of laser flash have been described in detail elsewhere[1][7][8]; we will therefore limit our description here to an outline of the principles and procedures, to serve as introduction to the ensuing discussions.

A typical apparatus used for laser flash measurements is shown in **Fig. 1**. The sample to be measured takes the form of a disk pellet, 8~10 mm in diameter and 1~3 mm thick. At the center of its back surface is fixed a set of fine thermocouple wires (<0.05 mm dia.) by means of silver-paste or welding.

The experimental procedure is as follows. A pulse of laser irradiation is impinged on the front surface of the sample maintained at a predetermined temperature. The temperature
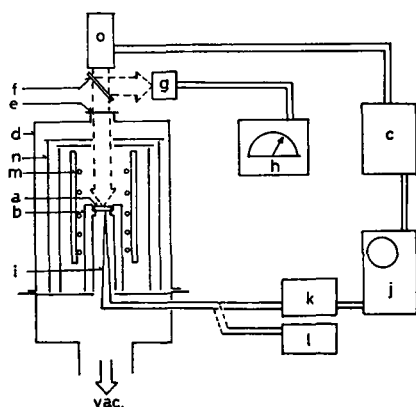
(a) Specimen, (b) Specimen holder, (c) Trigger and power supply, (d) Vacuum container, (e) Quartz window, (f) Reflecting glass, (g) Si-photoelectric cell, (h) Laser power meter, (i) Thermocouple, (j) Oscilloscope or transient recorder, (k) Preamplifier, (l) Millivolt-meter, (m) Furnace, (n) Reflecting plates, (o) Laser head

**Fig. 1** Block diagram of apparatus for measurements with laser flash method

history of the back surface of the sample is detected by the thermocouple mentioned above and recorded by oscilloscope or transient recorder. Some examples of the recorded temperature history are shown in **Fig. 2**. If the experiments are performed with sufficient care, the curve thus obtained should be quite similar in form to that shown in **Fig. 3**, which is calculated under the assumptions[1] that :—

(1) —the specimen is thermally insulated and is not transparent;

(2) —the duration of laser irradiation is insignificant compared with the time taken by the specimen for temperature rise;

(3) —the energy of the laser irradiation is absorbed by the thin surface layer uniformly over the whole area, and the ensuing heat flow is one-dimensional.
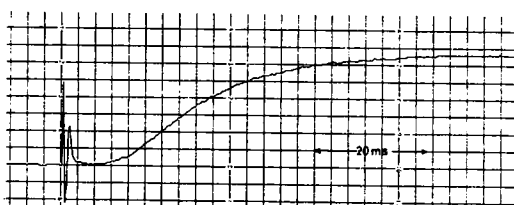
If the experimental conditions satisfy the above assumptions, then the thermal diffusivity of the specimen α (cm^{2}sec^{-1}) is given by

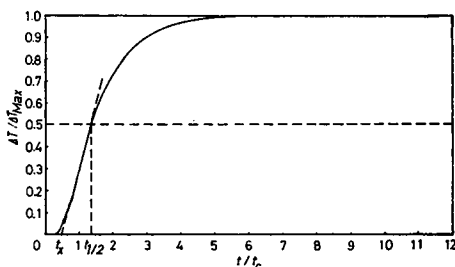$$\alpha = \frac{1.37 L^2}{\pi^2 t_{1/2}}, \qquad (1)$$

where L (cm) is the thickness of the specimen, and $t_{1/2}$ (sec) the lapse of time for the back-surface temperature to reach half its
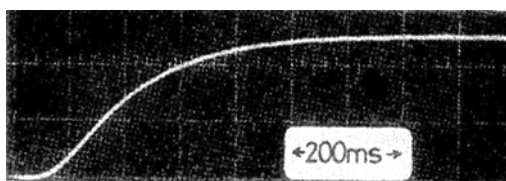
(a) By oscilloscope

(b) By trasient recorder

Fig. 2 Back-surface temperature history of specimen

ΔT: Temperature rise, ΔTmax: Maximum temperature rise, t: Time, t_c: Characteristic time $(t/t_c=1.37$ at $t=t_{1/2})$

Fig. 3 Calculated temperature-history of back surface of specimen

maximum temperature rise. The thermal conductivity K (W cm^{-1} K^{-1}) is calculated from the data of thermal diffusivity and specific heat capacity by the well-established relation

$$K=\alpha C_p\rho, \qquad (2)$$

where C_p (J g^{-1} K^{-1}) is the specific heat capacity and ρ (g cm^{-3}) the density of the sample. Thus, the heat capacity—which itself is one of the most important thermodynamic properties —plays a significant role in the determination of thermal conductivity.

The specific heat capacity C_p is also determined from the curve of Fig. 2 by the formula

$$C_p=\frac{Q}{\rho L \Delta T_{\text{max}}}, \qquad (3)$$

where Q (J cm^{-2}) is the energy density absorbed by a unit surface area of the specimen and ΔT_{max} (K) the maximum temperature rise. The value Q in Eq. (3) is determined by calibrating with a standard sample of known heat capacity.

2. Improved Laser Flash Method for Heat Capacity Measurement

Use of the laser flash method has not been as widely applied in measurements of heat capacity as in those of thermal diffusivity. This is due to a number of experimental difficulties which have impaired the reliability of the data obtained with this method. In fact, the data for US at 800 K reported by Moser & Kruger[3] in their pioneering work with this method were found to differ by about 10% from those obtained later by means of the drop method[9]. One of the main difficulties encountered in these earlier works was in measuring accurately the energy density of the laser beam absorbed by the sample. This problem was solved[8] by using a measuring system consisting of reflecting glass and photoelectric cell. Murabayashi *et al.*[8] determined by this means the heat capacity of Al$_2$O$_3$ at temperatures between 300 and 1,000 K within a deviation of ±1.5% from the NBS standard data[10]. The heat capacity of UN from 300 to 1,000 K was also determined[11] with the same precision, and the data were later confirmed to be in good agreement with those obtained by the drop method[12][13].

Another problem encountered with this method was the difficulty in determining the absolute heat capacity of an unknown sample, due to differences in the absorption efficiency of the laser energy, which depends on the reflectivity of the surface, and which hence varies with the sample. This problem also was successfully solved by utilizing an "absorbing disk"[6]. These improvements to laser flash calorimetry[14] have permitted the heat capacity of solid samples to be measured within a precision of ±0.5% in the range from 80 to 700 K, and within ±2% from 700 to 1,100 K.

Some details of the improved method pro-

posed by the present authors[6][14] are summarized below. A schematic diagram of the apparatus used for the improved method is shown in **Fig. 4**[6]. The samples to be measured usually take the form of small disks. An absorbing disk of glassy carbon 12 mm in diameter and 0.2 mm thick, weighing about 50 mg, is laid on the sample surface and bonded with a very small amount ($\approx$1 mg) of grease. This disk serves to absorb the impinging laser energy. The arrangement is shown in **Fig. 5**[6]. The advantages of this
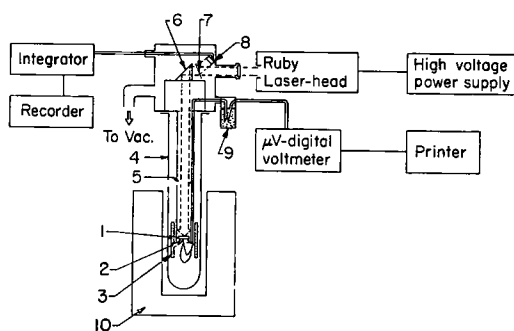
(1) Specimen, (2) Thermocouple (Cu-constantan), (3) Internal heater, (4) Quartz container, (5) Adjusting slit, (6) Prism, (7) Reflecting glass, (8) Si-photoelectric cell, (9) Ice bath, (10) Outer heater or liq. N₂ bath

Fig. 4 Improved apparatus for heat capacity measurement by laser flash method

(1) Laser beam, (2) Specimen, (3) Thermocouple, (4) Colloidal graphite, (5) Absorbing disk (glassy carbon), (6) Silver-paste
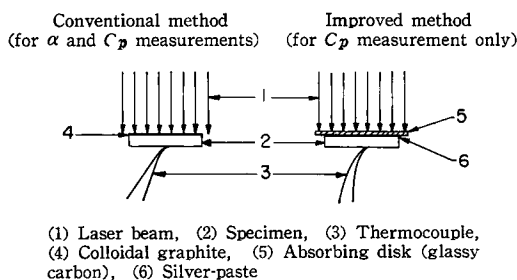
Fig. 5 Absorbing disk and arrangement thereof

absorbing disk are that : (1) It receives the whole flux of the laser beam, as shown in Fig. 5. This assures good reproducibility of results without any difficulty as compared with the conventional method. (2) It eliminates differences in surface absorption efficiency between different samples. This makes it possible to determine the absolute heat capacity of an unknown sample. (3) It permits heat capacity measurements to be made

in the temperature region of the phase transition of a sample. An example is shown in Fig. 15[14], Sec. IV-1, for the case of UP with a sharp transition of heat capacity at 121 K. (4) Heat capacity measurements become possible on powdered or liquid samples[15] by using an absorbing disk and a small sample container.

In the improved method, the molar heat capacity, C_p (J mol⁻¹ K⁻¹), is given, instead of Eq. (3), by the expression

$$C_p = \frac{1}{m}\left(\frac{E}{\Delta T_{\max}} - C\right),\qquad(4)$$

where E (J) is the total energy of the laser flash absorbed by the absorbing disk, m (mol) the quantity of the sample, and C (J K⁻¹) the heat capacity of the absorbing disk including that of the grease used for bonding.

It should be pointed out that the improved method does not provide for determining the thermal diffusivity simultaneously, because of the presence of the absorbing disk. The thermal diffusivity can be measured by the conventional method already described, by using the same apparatus but without the absorbing disk.

3. Thermal Diffusivity Measurement

This section deals with some of the important experimental conditions for obtaining reliable data on thermal diffusivity[16]. In order to measure the thermal diffusivity with good precision, the following requirements must be satisfied.

(1) One-dimensional heat flow : The laser beam is required to irradiate uniformly the whole front surface of a specimen. Thus, the specimen must have a diameter slightly smaller than that of the laser beam. **Figure 6** shows typical examples of the $\Delta T - t$ curve[17] when this requirement is not satisfied.

(2) Choice of optimum thickness of specimen : A specimen which is too thick would entail significant radial heat loss. Conversely, if too thin, it would no longer permit neglect of the duration of laser-beam irradiation. The optimum thickness would appear to be one that results in
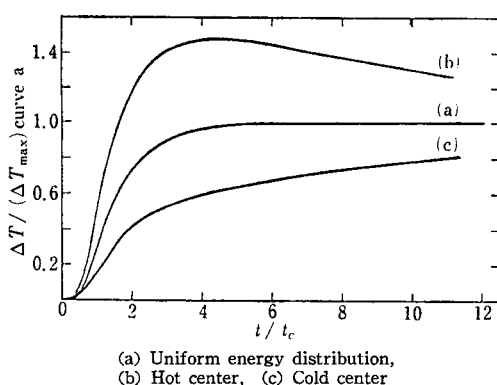
(a) Uniform energy distribution,
(b) Hot center, (c) Cold center

Fig. 6 Response of back-surface temperature

$t_{1/2} = 70 \sim 150$ msec.

(3) Thermal insulation of specimen :
   The use of an excessively thick thermo-couple would cause distortion in $\Delta T - t$ curve, because of the heat loss along the thermocouple and of its extra heat capacity. For these reasons, a thermocouple of diameter smaller than 50μm was used in our laboratory.

(4) Effective thermal contact between thermocouple and specimen : To assure good contact, spot-welding is advisable for a metallic sample. In the case of ceramic samples, silver-conductive paste is used in the authors' laboratory. Thermal contact resistance between thermocouple and specimen is usually negligible, unless the specimens are very thin. A practical means of verifying whether the requirements (1) $\sim$(4) have been satisfied is to compare the $\Delta T - t$ curves between experiment (Fig. 2) and calculation (Fig. 3).

(5) Accurate record of the temperature history of the back surface of the specimen : The use of low-noise pre-amplifier and a transient recorder has proved to give better results than possible by oscilloscope (see Fig. 2).

(6) Correction to account for finite duration of laser pulse : The effect of the finite duration of the laser pulse and its correction have been discussed by many authors[18]~[20]. In the present instance, with a laser pulse of 1 msec of shape assumed to be triangular, the relevant

correction required for thermal diffusivity, for example, is less than 1% with specimens of $t_{1/2} \approx 50$ msec.

(7) Determination of appropriate effective temperature : The laser irradiation on the front surface of the specimen instantaneously raises the temperature in a thin layer of the specimen near this surface and a large temperature gradient is produced in the specimen. Hence, the concept of an effective temperature is necessary. Parker *et al.*[1] have given for this effective temperature the expression

$$T_e = T_0 + 1.6 \Delta T_{max}, \qquad (5)$$

assuming a simple linear temperature gradient. Kamimoto *et al.*[16], on the other hand, have calculated the temperature distribution from the theoretical equation of heat conduction, with the results shown in **Fig. 7**. This yields an effective temperature of

$$T_e = T_0 + 0.99 \Delta T_{max}, \qquad (6)$$

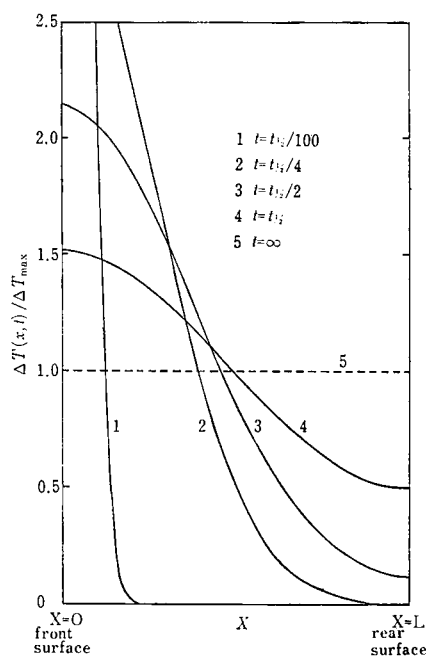where T_0 is the initial temperature of the specimen.

Fig. 7 Model of temperature distribution in specimen caused by laser flash

The above considerations are mainly relevant to measurements at temperatures below 1,000 K, where a thermocouple is used to measure the temperature. At higher temperatures, other problems must also be considered, such as to assure accurate temperature measurement and correction for radiation loss.

## III. CERAMIC OXIDES AND MIXED OXIDES FOR NUCLEAR APPLICATIONS

Uranium dioxide and mixed oxides such as $(U, Pu)O_2$ are today the most widely used nuclear fuel materials, despite their characteristically low thermal conductivity. The effects of the composition and stoichiometry of these oxide fuel materials on their thermal conductivity are the important knowledge essential in the nuclear technology. Furthermore, fission products in the form of solid solutions and two-phase mixed oxides result in the decrease of their thermal conductivities.

In this chapter, we will review the studies made in the past on thermal diffusivity measurements by the laser flash method on several systems of nuclear oxides and their mixed oxides below 1,000 K. Also, a brief discussion will be presented on some theoretical models proposed for ceramic solid solutions to explain their thermal conduction behavior.

### 1. Experimental Results Obtained by Laser Flash Method

The thermal conductivities of UO_2 and U_4O_9 at temperatures from 100 to 300 K undertaken by Kamimoto *et al.*[21] are presented in **Fig. 8**, where the data for UO_2 by Moore & McElroy[22] are also given for comparison. The small discrepancy seen between both data might be mainly due to differences in the amounts of impurities contained in the samples. These data agree fairly well with those extrapolated from the measurements by Godfrey *et al.*[23] at higher temperatures.

Figure 9 presents the measured thermal
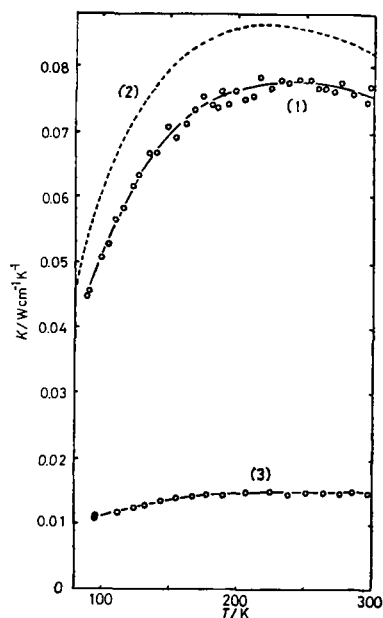
(1) UO_2 (Kamimoto *et al.*[21]), (2) UO_2 (Moore & McElroy[22]), (3) U_4O_9 (Kamimoto *et al.*[21])

**Fig. 8** Thermal conductivity of UO_2 and U_4O_9
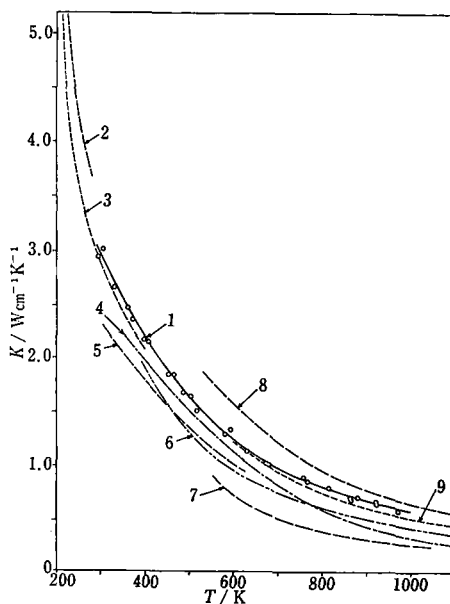
(1) Murabayashi *et al.*[24] (open circles: 1.4%, corrected to the theoretical density), (2) De Goer[27] (1.4%), (3) Burk[25] (4.4%). (4) Francle & Kingery[28] (5~10%), (5) Powell *et al.*[29] (0.7%), (6) Elston *et al.*[30] (corrected to theoretical density), (7) Fitzsimmons[31] (2%), (8) Emanuelson[32] (2%), (9) Taylor[26] (1%). Figures in parenthesis indicate the porosity of the sample.

Fig. 9 Thermal conductivity of BeO

conductivity of BeO[24] with laser flash together with those reported in literature. Curve 1 agrees with the values by Burk[25] at lower temperatures and with those by Taylor[26] at higher. It also shows agreement with the values by Francle & Kingery[28], when account is taken of the difference in porosity of the samples.

Weilbacher[33] measured the thermal diffusivity of ThO_2 by means of the laser flash at temperatures from 750° to 2,700°C and by the Ångström method at temperatures from 100° to 750°C. The thermal diffusivity of ThO_2 was also measured by Murabayashi *et al.*[7][34] at temperatures of 20° to 1,000°C. The results agree with the data by Weilbacher with laser flash, considering the difference in porosity.

The thermal conductivity of ThO_2-UO_2 mixed oxides were measured with laser flash by Murabayashi *et al.*[7][34], Ferro *et al.*[35][36] and Matolich & Storhok[37], while Gibby[38] measured that of PuO_2-UO_2. The data for the ThO_2-UO_2 solid solution system are presented in **Fig. 10**, in which the three sets of data show reasonable agreement with each other.
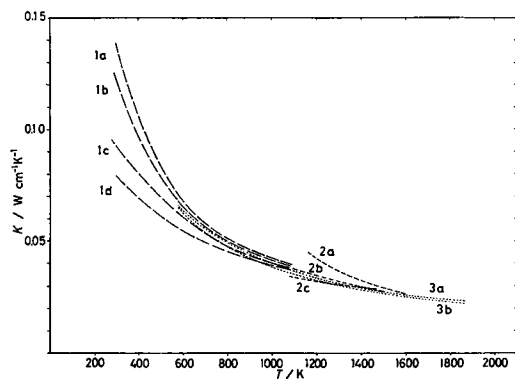
curves 1a~1d: Murabayashi[34], (1a: ThO_2, 1b: ThO_2-1 mo% UO_2, 1c: ThO_2-5% UO_2, 1d: ThO_2-10% UO_2) (corrected to 95% T.D.); curves 2a~2c: Ferro *et al.*[35][36], (2a: ThO_2-1% UO_2, 2b: ThO_2-4% UO_2, 2c: ThO_2-10% UO_2); curves 3a, 3b: Matolich & Storhok[37] (3a: ThO_2-3.2% UO_2, 3b: ThO_2-10% UO_2) (95.6% T.D.).

Fig. 10 Thermal conductivity of ThO_2-UO_2 solid solutions

For the ThO_2-BeO two phase system the thermal conductivity was determined at temperatures from 300 to 1,000 K[24]. The results

are presented in **Fig. 11**, together with curves based on the theoretical model for two phase system[24][40]. A noticeable difference is seen between the experimental data and the values expected from the model at compositions rich in BeO. This might be attributed to the irregular shape and distribution of the second phase—namely the ThO_2 particles.
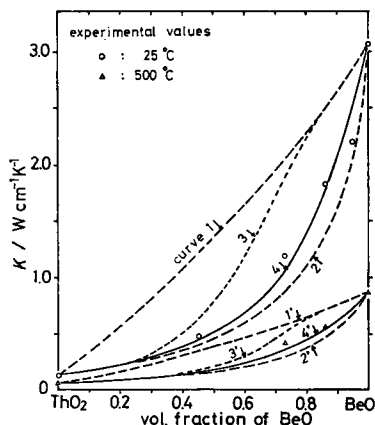
curves 1: estimated thermal conductivity of a sample of an extreme case in which the continuous phase has higher thermal conductivity than the other phase[40]; curve 2: the continuous phase has lower thermal conductivity[40]; curve 3: estimation from Kingery's model[40]; curve 4: estimation from a modified Maxwell model[69][70]. Curves 1~4 represent value at 25°C, curves 1'~4' those at 500°C.

Fig. 11 Thermal conductivity of ThO_2-BeO mixed oxides—experimental results[24] and calculated curves based on several models

2. Theoretical Models for Ceramic Solid-solutions

The effect of impurities on the thermal conductivity of non-conductive solids is formulated from the concept of mean free path by the equation[40][41]

$$\frac{1}{K} = a + bT, \qquad (7)$$

where K is the thermal conductivity, T the temperature, while a and b are constants to be determined experimentally. The relation indicates that, above the Debye temperature, the mean free path due to thermal scattering alone is inversely proportional to the temperature, whereas that due to impurity scattering alone can normally be assumed temperature independent. The above ex-

pression (7) has been confirmed from experiments to be a good approximation for various substances.

Equation (7), however, does not express very well the quantitative relation between the thermal conductivity and the content of impurities in the sample. Relaxation time theory was first introduced by Klemens[42] and Callaway[43] for the thermal conductivity of the samples containing impurities or isotopes at low temperatures. The theory was then extended to corresponding phenomena at higher temperatures, namely the isotope effect on the thermal conductivity of Ge at temperatures up to 300 K[44], and of the Ge-Si solid solution system at 80 and 300 K[45]. In these cases the scattering was thought to be mainly due to the mass-difference effect between the guest and the host (lattice) atoms. Subsequently, Abeles[46] took into account also the effect of strains generated in the lattice of alloys such as Ge-Si and (Ga, In)As. According to this theory the scattering of phonons in the mixed substances depends on a scattering cross section Γ, which is expressed by

$$\Gamma = x(1-x)\left[\left(\frac{\Delta M}{M}\right)^2 + \varepsilon\left(\frac{\Delta \delta}{\delta}\right)^2\right], \qquad (8)$$

where x is the composition, $\Delta M = M_A - M_B$, $\Delta \delta = \delta_A - \delta_B$ (δ^3 = mean atomic volume), $M = xM_A + (1-x)M_B$, and ε is a parameter representing the magnitude of the strains of the lattice, while M_A and M_B are the atomic weights of atoms A and B, respectively. The thermal conductivity of mixed substances is then expressed as a solution[43][46] of the Boltzmann equation for phonons containing Γ. This theory has permitted successful explanation of the thermal conductivity of Ge-Si and (Ga, In)As systems[46].

Murabayashi[34] has applied the above concept to the thermal conductivity of ThO_2-UO_2 and ThO_2-CeO_2 systems, and Gibby[38] has done the same for the UO_2-PuO_2 system. An example of the results is shown in **Fig. 12**, which illustrates the dependence of the thermal conductivity of ThO_2-UO_2 system on its composition. As mentioned above, the theory explains well the factors that determine the thermal resistance of mixed oxide ceramics.
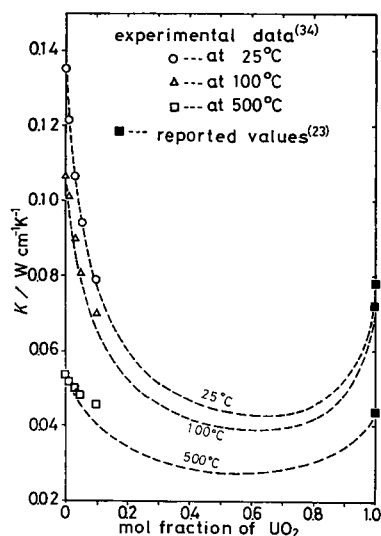

Dotted curves represent estimated values for the full range of compositions at 25°, 100° and 500°C on the basis of the experimental values at 25°C.

Fig. 12 Composition dependence of thermal conductivity of ThO_2-UO_2 solid solutions[34]—experimental results and estimated values

However, the resulting equation contains parameters such as the Debye temperature and the scattering rate of N- to U-processes, which are in some cases not yet well determined.

More recently, Murabayashi *et al.*[71] have obtained experimentally the relation between the thermal conductivity and the scattering cross section Γ, as shown in **Fig. 13**. The
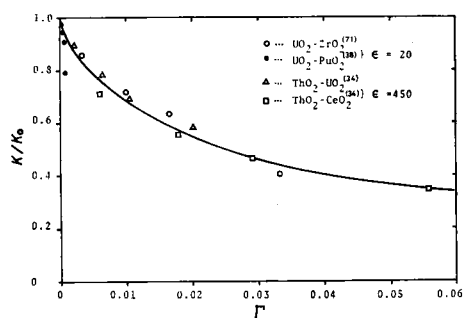
K: Thermal conductivity of the solid solution;
K_0: Thermal conductivity of the pure oxide, (UO_2 or ThO_2)

Fig. 13 Dependence of thermal conductivity of ceramic solid-solutions on Γ[71]

relation is based on the assumption that solid solutions belonging to a common type would have a common value of ε in Γ. As seen in Fig. 13, the assumption is found to hold for the solid-solution systems containing UO_2 or ThO_2. The foregoing attempts to correlate the experimental results with theoretical models appear to be promising, but further examination in more detail is called for, on the basis of much additional data, which can now be expected from precise laser flash measurements.

IV. URANIUM COMPOUNDS OF NaCl TYPE

Increasing necessity is being felt for extensive and accurate knowledge of the thermal properties of NaCl-type uranium compounds, especially at high temperatures. The laser flash method for heat capacity measurement has proved its usefulness in obtaining reliable data on nuclear materials as described below, and it has now become possible to analyze these heat capacity data in terms of electronic (Schottky) contribution[14].

Uranium compounds of NaCl-type are characterized by high electrical and thermal conductivities, which qualify them as promising materials for fast reactor fuel. The mechanism of thermal conduction of these compounds is interesting, in that both electrons and phonons contribute to the thermal energy transport. The recent advances seen in methods of laser flash measurement in the range of 80~1,000 K have made it possible to analyze the measured thermal conductivity of these compounds and their solid solutions and distinguish between phonon and electronic thermal conductivities.

The results of such measurements made by laser flash method are presented below.

1. UC, UN, UP and US

Among the NaCl-type uranium compounds, those listed in the above heading have been studied extensively by the laser flash method.
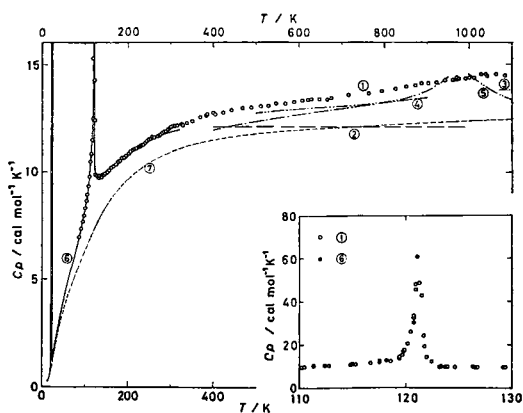
(1) Heat Capacity

Moser & Kruger[3] have measured the

heat capacities of UC, UP and US from 300 to 900 K. In the case of UC, the data agreed fairly well with those[47] measured by the drop method. The data for UP and US, however, do not agree with those obtained more recently. The heat capacity of UN was measured by laser flash from 300 to 1,000 K by Takahashi *et al.*[11], which has proved to accord well with the newer data of Oetting & Leitnaker[12], as shown in **Fig. 14**. Murabayashi *et al.*[48] have reported heat capacity data on US in the same temperature range, which compare well with data obtained by the drop method[9]. Quite recently, Yokokawa *et al.*[14] have given the heat capacity
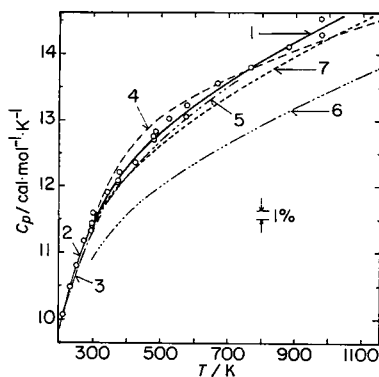
(1) Takahashi *et al.*[11], (2) Westrum & Barber[61], (3) Counsell *et al.*[62], (4) Blank[63], (5) Cordfunke & Muis[13], (6) Harrington[64], (7) Oetting & Leitnaker[12]

Fig. 14 Heat capacity of UN

(1) Yokokawa *et al.*[14], (2) Moser & Kruger[3], (3) Brugger[65], (4) Ono *et al.*[66], (5) Men'shikova *et al.*[67], (6) Counsell *et al.*[49], (7) Estimated lattice heat capacity[14]

Fig. 15 Heat capacity of UP

of UP from 80 to 1,100 K, which is shown in **Fig. 15**. From 80 to 300 K the results agree very well with those from adiabatic calorimetry by Counsell *et al.*[49], including the values near the antiferro-paramagnetic transition near 121 K. At higher temperatures, there are no reliable data obtained by other methods to be compared with.

(2) Thermal Diffusivity and
        Thermal Conductivity

The thermal diffusivity values of UC and UN have been measured by laser flash from 100 to 1,000 K by Kamimoto *et al.*[50] and Takahashi *et al.*[11]. The thermal conductivity values derived from these measurements agree well with the data by other investigators[51][52].

Corresponding data for UP and US have also been determined from 100 to 1,000 K by Kamimoto *et al.*[53] These results are about 10% higher than those reported by Moser & Kruger[3] in their pioneering work, but the temperature dependence revealed in these two different studies are very similar to each other. At the temperatures of the reported magnetic transition—121 K for UP and 180 K for US—the measured thermal diffusivities show sharp minima. These thermal conductivity data for UP and US have been calculated from heat capacity data obtained by the laser flash method[14][48], and are as presented in **Fig. 16**, together with those of UC and UN. The results for UP are higher than those obtained by Dunworth[54], while that for US agrees with that obtained by Lawroski *et al.*[55]
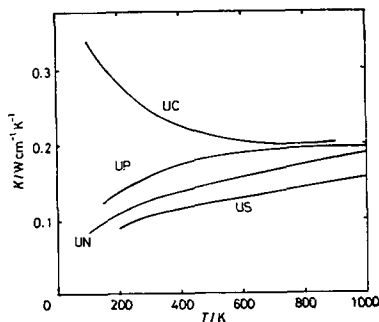
2. U(C, N) and U(P, S) Solid Solutions

The thermal diffusivity has been measured on $UC_{1-x}N_x$ of several compositions from 100 to 1,000 K by Kamimoto *et al.*[50] The thermal conductivity was derived therefrom by assuming additivity of the heat capacity in solid solutions. The resulting values of thermal conductivity are shown in **Fig. 17**, plotted against composition, for several temperatures from 100 to 900 K. It is seen that the thermal conductivity of solid solutions is distinctly lower than that of UC, and falls quite close to that of UN. The curves for different temperatures each have a minimum at different compositions. Below 200 K the conductivity is smallest for pure UN. With increasing temperature above 300 K, the minimum point moves toward higher carbon content. This tendency agrees with the results reported by Pascard[56]. The behavior was explained[50] in terms of the temperature dependence of the phonon (K_p) and electric (K_e) components, which were separated by assuming constant Lorenz number. It was found that K_e decreases smoothly with increasing nitrogen
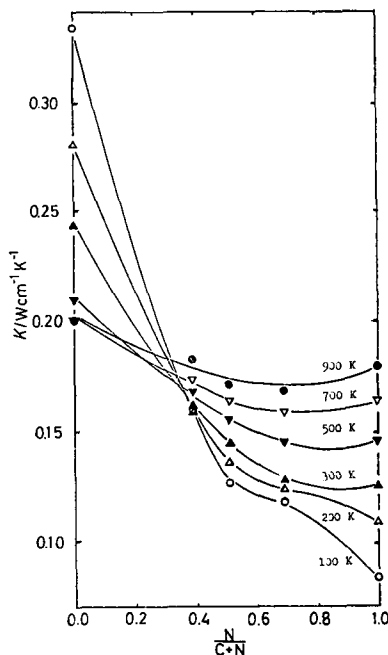
Fig. 16 Thermal conductivity of NaCl-type uranium compounds (Kamimoto[68])

Fig. 17 Composition dependence of thermal conductivity of $UC_{1-x}N_x$ (Kamimoto *et al.*[50])

content in the temperature range investigated, whereas the curves for K_p, as shown in **Fig. 18**, pass through a minimum at an intermediate composition above 300 K. The decrease in K_p of UN at 100 K may be attributed to the scattering of phonons by disordered magnetic moments.
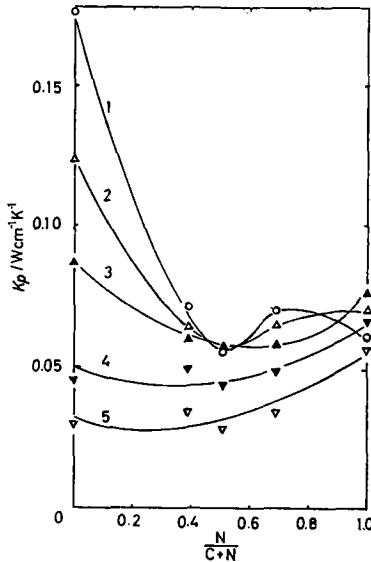

Fig. 18 Lattice component of thermal conductivity of $UC_{1-x}N_x$ (Kamimoto *et al.*[50])

The thermal diffusivity of $UP_{1-x}S_x$ solid solutions has also been measured by Kamimoto *et al.*[67] from 300 to 1,000 K. The composition dependence of the thermal conduc-
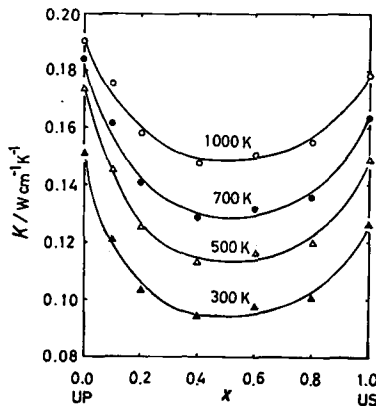

Fig. 19 Composition dependence of thermal conductivity of $UP_{1-x}S_x$ (Kamimoto *et al.*[68])

tivity of $UP_{1-x}S_x$ derived from these data is shown in **Fig. 19**, which shows a deeper drop at intermediate compositions than in the case of $UC_{1-x}N_x$. This is due to the larger K_p decrement at intermediate compositions and a larger value of K_p/K_e for $UP_{1-x}S_x$ than for $UC_{1-x}N_x$.

V. CONCLUSIVE REMARKS

In this article, we have reviewed experimental techniques adopted in the laser flash method at temperatures from 80 to 1,000 K and its applications to some nuclear materials. The subjects treated were mainly taken from experience accumulated in the authors' laboratory, and it should be noted that this review is not exhaustive.

We are convinced that the laser flash method is a most useful tool for investigating the thermal properties of nuclear materials, provided sufficient care is taken to realize suitable experimental conditions. It should be noted, however, that there still remain many problems to be solved in applying this technique. The more immediate applications still to be established include thermal diffusivity measurements on liquid[68] or powder samples and on transparent samples, and heat capacity measurement at temperatures above 1,000 K. Another domain remaining to be explored for nuclear materials is the effect of porosity on the thermal conductivity, including its temperature dependence[59][60], for which the laser flash method could provide a convenient and accurate means.

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