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Measurement of the Thermal Diffusivity of Molten KCl up to 1000°C by the Forced Rayleigh Scattering Method[1]

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This paper describes measurement of the thermal diffusivity of molten KCl in the temperature range from 804 to 1030°C by the forced Rayleigh scattering method. In this contact-free optical measuring technique for the thermal diffusivity of liquids, a sample needs to be colored by the admixture of a dye for suitable absorption of a heating laser beam. The dye substances employed are $CoCl_2$ and $NiCl_2$, which were chosen through the experimental evaluation. The accuracy is estimated to be $\pm 7\%$ for molten KCl colored with $NiCl_2$. The results converted to thermal conductivity show one of the smallest values among other previous data; the difference is a factor of four. The present study demonstrates the promising applicability of the forced Rayleigh scattering method to the measurement of high-temperature molten salts, which has never be attained by other conventional methods.

KEY WORDS: high temperature; KCl; molten salts; forced Rayleigh scattering method; thermal conductivity; thermal diffusivity.

1. INTRODUCTION

Because of the recent rapid progress of the material sciences, the needs for thermophysical property data of new materials are increasing and also the range of measuring condition is expanding more extensively than ever before. However, it is often encountered that widely used conventional methods are absolutely inappropriate for such materials and conditions, owing, for example, to anisotropy, scarcity, shape, and toxicity of samples or extreme high/low temperatures and pressures. It is therefore expected to develop new measuring techniques for thermophysical properties which

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meet the demand for new materials and for severe measuring conditions. As a potential technique to meet such requirements, we have been exploring the forced Rayleigh scattering method, which is an optical measurement technique for the thermal diffusivity of materials [1, 2].

The distinguishing features of the forced Rayleigh scattering method for the thermal diffusivity measurement are summarized as follows. (i) The method has an advantage in the case when it is difficult to insert sensors in a sample such as high-temperature corrosive melts because of its basic feature of contact-free measurement. (ii) The influence of natural convection is negligible, since the measuring time is very short (typically within 1 ms). (iii) The temperature rise during measurement is very small (less than 0.1 K), thus the error due to radiation may not be significant even at high temperatures. (iv) A sample volume of only a few cubic millimeters is required, which enables the measurement of valuable samples and which is also advantageous at high temperatures. (v) The method is suitable for measurement of anisotropic materials such as liquid crystals. Because of the above-mentioned features, the forced Rayleigh scattering method seems capable of surpassing the other conventional measurement techniques for thermal diffusivity (or thermal conductivity). In the present paper, we extend the range of applicability of the forced Rayleigh scattering method to high-temperature molten salts.

2. PRINCIPLE OF MEASUREMENT

The principle of the forced Rayleigh scattering method is shown schematically in Fig. 1. Two pulsed high-power laser beams of equal intensity cross an absorbing sample at an angle θ. They generate an optical interference fringe with a spatially sinusoidal intensity distribution. By absorbing the laser light, this interference pattern induces a corresponding temperature distribution in the x direction in the sample. After the heating process, the excited temperature distribution exponentially relaxes by the heat conduction process. If (i) the grating period Λ is much smaller than the sample thickness, (ii) Λ is sufficiently small compared with the light absorption length, and (iii) Λ is small enough compared with the diameter of the heated area, then the assumption of one-dimensional heat conduction in the x direction is permissible. Consequently, this decaying process can be described by

$$T(x, t) = T_0 + \Delta T_0[1 + \cos qx \exp(-t/\tau)] \tag{1}$$

where T is the temperature, t the elapsed time after heating, T_0 the initial temperature, ΔT_0 the initial spatial temperature amplitude, and $q = 2\pi/\Lambda$

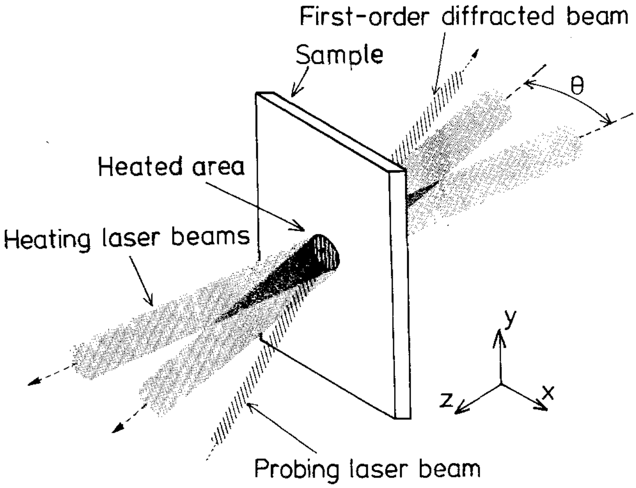

Fig. 1. Principle of the forced Rayleigh scattering method.

the wave number of the interference pattern. Equation (1) indicates that the spatial temperature amplitude decays exponentially with the relaxation time of heat conduction τ,

$$\tau = (1/a)(\Lambda/2\pi)^2 \tag{2}$$

The spatially periodic temperature distribution produces a corresponding refractive index distribution which acts as an optical phase grating on a low-power probing laser beam of nonabsorbed wavelength in the sample. Adopting the theory of diffraction, the thermal diffusivity is determined by detecting the temporal decay of the first-order diffracted probing beam I_1, written as

$$a = -(\tfrac{1}{2})(\Lambda/2\pi)^2 \, [d \ln I_1(t)/dt] \tag{3}$$

Therefore, we can determine the thermal diffusivity a by measuring the time dependence of I_1 (equivalently τ) and the grating period Λ. More detailed theory has been described elsewhere [1].

3. EXPERIMENTAL APPARATUS

Figure 2 displays the present experimental apparatus. The heating laser is a single-mode argon-ion laser (wavelength, 514.5 nm; 1.8 W) and its continuous light is chopped by a rotating mechanical chopper to generate a short pulse. The heating pulse duration time can be changed from 1 to

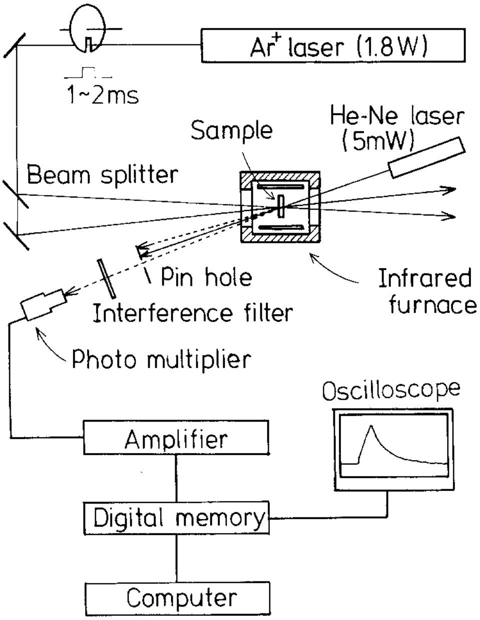

Fig. 2. Experimental apparatus.

2 ms. The heating lasers, divided into two beams of equal intensity by means of a beam splitter, intersect in the sample to produce the interference pattern. A He–Ne laser (wavelength, 632.8 nm; 5 mW) is employed for probing the relaxation of the temperature distribution. The first-order diffracted beam is detected by a photomultiplier through a pinhole of 500-μm diameter and an interference filter. The output from the photomultiplier is recorded by a digital memory (12 bits; sampling time, 5 μs) and is transferred to a computer.

A sample cell is made of two quartz glasses (15×18 mm; thickness, 1 mm) with spacers. The thickness of the sample layer is fixed (about 1 mm) by employing quartz glass spacers which are welded onto cell walls with the aid of a microtorch. The amount of sample needed for this cell is only 0.2–0.3 g. An infrared furnace is utilized for the measurement at high temperatures because it readily heats up a small amount of sample and also ensures the optical path of the laser beams. It should be noted that the surface of the cell wall is painted by a high-emissivity coating excluding the laser spot area in order to secure enough absorption of infrared light from the furnace. Temperature is measured with a thermocouple (Type K) enclosed in a cell holder, since it is difficult to insert the thermocouple directly into the sample. Thus the accuracy of temperature measurements is estimated to be ±15°C, which is not so inferior taking into account the weak temperature dependence of the thermal diffusivity of molten salts. Finally, the grating period is determined by means of a CCD image sensor which has been described in Ref. 1.

4. RESULTS AND DISCUSSION

In this method, the sample needs to be colored by the addition of a dye for suitable absorption of the heating laser beam. Since high-temperature molten salts are normally transparent, it is necessary to find appropriate dye substances which possess the following properties: (i) an absorption band at the wavelength of the argon-ion laser but transparent to the wavelength of the He–Ne laser in the present apparatus (the color generally seems red); (ii) a large enough absorption coefficient with no detectable effects on the thermal diffusivity; and (iii) solubility in molten salts and stability at high temperatures. We could not find any previous studies on the coloration of molten salts, thus we performed trial-and-error experiments by employing the candidate substances of dye for molten KCl listed in Table I. Most of the substances listed include transition metal ions which have an absorption band in the visible-light wavelength and are stable at high temperatures. In Table I, X indicates that no visible color was seen by the admixture of the substance or the substance reacted with the molten salt at high temperatures. Among the substances marked △, $Nd(NO_3)_3$ was very stable but the absorption was not enough for measurement. Although V_2O_5 exhibited a strong enough red together with Fe_2O_3 as an oxidizing agent, the chemical reaction with salt was strong. Even though the substances indicated by ○ did not work as perfect dyes, it was possible to measure the thermal diffusivity by adding a small amount

Table I. Dye Substances Tested for Molten KCl

Ion	Dye substance	Coloring ability
Co^{2+}	Co_3O_4	X
	$CoCl_2$	○
	$Co(NO_3)_2$	X
Ni^{2+}	$NiCl_2$	○
	$NiSO_4$	○
Mn^{3+}	MnO_2	X
	$MnCl_2$	X
V^{5+}	V_2O_5	△
Nd^{3+}	$Nd(NO_3)_3$	△
CdS (colloid)	CdS	X

of them in molten KCl. $CoCl_2$ showed a bluish color with a weak absorption of the argon-ion laser. On the other hand, $NiCl_2$ and $NiSO_4$ also exhibited a bluish color but the absorption was strong enough.

In order to show how the absorption coefficient of dye affects the signal-to-noise ratio of detected light signals, Fig. 3 indicates typical diffracted light signals for molten KCl with the admixture of 1 wt% of $CoCl_2$ and $NiCl_2$, respectively. As can be seen, in the case of employing $NiCl_2$ as a dye, the intensity of the diffracted beam is stronger in comparison with the case of $CoCl_2$, thus the accuracy of the decay time constant is much better. Consequently the selection of an appropriate dye substance is one of the keys to the present study. We did not examine the absolute absorption coefficient of dye substances, since our first aim here was to demonstrate the strong applicability of the forced Rayleigh scattering method to high-temperature melts. For a more exact setting of the measuring conditions for other molten salts, further study on this subject is needed.

Table II contains the present experimental results for the thermal diffusivity of molten KCl colored with $CoCl_2$ and $NiCl_2$ in the temperature range from 804 to 1030°C. The averaged values of 6 to 15 measurements at the same temperatures are tabulated. The sample employed had a stated

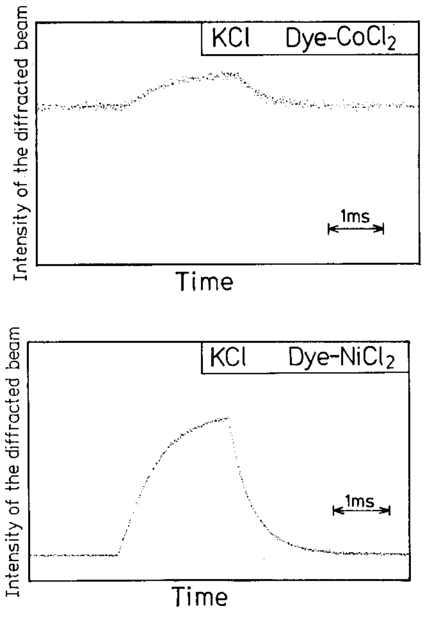

Fig. 3. Typical examples of detected light signals for different dye substances.

Table II. Measured Thermal Diffusivity of Molten KCl[a]

Dye	Temperature (°C)	Thermal diffusivity ($m^2 \cdot s^{-1}$)	Reproducibility (±%)
$CoCl_2$	804	2.15×10^{-7}	12
$NiCl_2$	874	2.34	4.2
	930	2.34	4.8
	1030	2.41	3.8

[a] For thermal conductivity calculation, ρ ($kg \cdot m^{-3}$) $= 1976.7 - 0.5831T$ (°C) [4], and C_p ($J \cdot kg^{-1} \cdot K^{-1}$) $= 984.6$ [5].

purity of not less than 99%. In these measurements, the grating period was 74.71 μm, the heating pulse duration time was 1.2 ms, and the interval between measurements at the same temperature was about 1 min. No previous studies were available for the thermal diffusivity of molten KCl, therefore Fig. 4 shows the thermal conductivity derived from literature data of the specific heat capacity [3] and the density [4] compared with other experimental results. The accuracies of the specific heat capacity and density are not recorded in the original papers but are estimated to be better than ±5% altogether. In Fig. 4, the symbol ★ indicates the present result colored with 1 wt% of $CoCl_2$, whereas ☆ indicates the result colored with 1 wt% of $NiCl_2$. Although the reproducibility with $CoCl_2$ dye was ±12% because of the weak light signals as mentioned before, in the case of $NiCl_2$ dye it was improved to better than ±5%. With regard to the absolute values, however, it seems that there is no meaningful differerence between the data obtained by two different dyes.

It should be particularly noted that the previous thermal conductivity values of molten KCl scatter from about 0.4 to 1.2 $W \cdot m^{-1} \cdot K^{-1}$ and their temperature coefficients are considerably large positive values. In contrast, the present results are the smallest of all and agree well with the data of McDonald and Davis [5] obtained with the transient hot-wire method using a platinum wire sheathed with a quartz tube. Moreover, the temperature dependence of the thermal conductivity exhibits an almost zero or weak negative. The data of Smirnov et al. [6], Fedorov and Machuev [7], and Polyakov and Gildebrandt [8] were all measured by the steady-state concentric cylinder method; it is thus considered that all these data are influenced strongly by the convection, radiation, and heat losses, all of which increase the apparent thermal conductivity. The present results converted into thermal conductivity are evaluated to be constant within the estimated accuracy and the mean value is 0.32_9 $W \cdot m^{-1} \cdot K^{-1}$ (804–1030°C). The assessment of accuracy for KCl (with $NiCl_2$)

measurement is similar to that presented in Ref. 1. The systematic error factors, effect of cell wall, effect of dye, and effect of Gaussian beam intensity distribution, are estimated to ±1%. The accuracy of the grating period is ±0.5% and that of the time constant is ±5%. Thus the overall accuracy is estimated to be ±7%.

We conclude that the forced Rayleigh scattering method can be applied to high-temperature molten salts with a moderate accuracy which had never been accomplished by any other conventional methods. We believe that by carrying out a more intensive survey of dye substances and by improving the apparatus, it may be possible to measure the thermal diffusivity of many other molten salts over a wider temperature range.

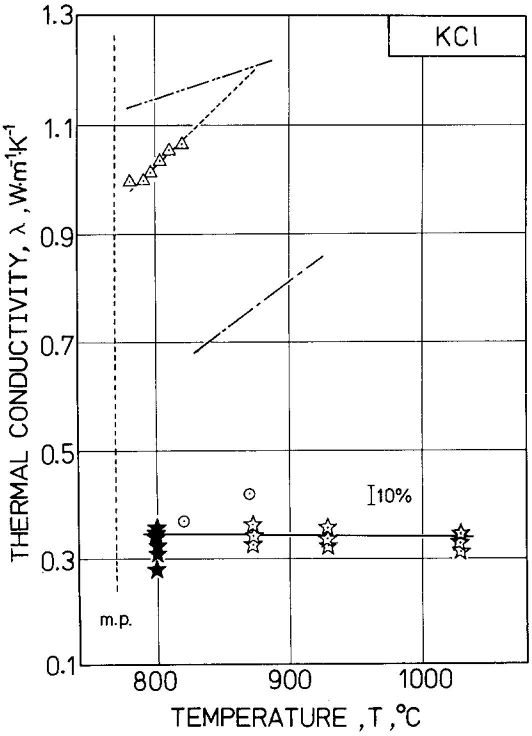

Fig. 4. Thermal conductivity of molten KCl: (——-·——) Smirnov et al. [6]; (⊙) McDonald and Davis [5]; (––––) Bystrai et al. [9]; (—-—) Fedorov and Machuev; (△) Polyakov and Gildebrandt [8]; (★) present work (dye, $CoCl_2$); (☆) present work (dye, $NiCl_2$). The present thermal diffusivity data are being converted into thermal conductivity.

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