

# **Experimental Determination of the Thermal Diffusivity of Molten Alkali Halides by the Forced Rayleigh Scattering Method. I. Molten LiCl, NaCl, KCl, RbCl, and CsCl**

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As a series of experimental determinations of the thermal diffusivity of molten alkali halides, this paper describes measurements on five molten alkali metal chlorides (LiCl, NaCl, KCl, RbCl, and CsCl) in the temperature range up to 1440 K by the forced Rayleigh scattering method.  $K_2Cr_2O_7$  is employed as a dye substance to color the transparent molten salts. The accuracy is estimated to be  $\pm 4$  to  $\pm 11\%$  depending on the measured salts. In comparison with the present results converted into thermal conductivity, most of the previous experimental data obtained by steady-state methods show larger values, up to about five times, which may be due to the systematic error caused by the presence of convection and radiation. It is found that the thermal conductivity of these series of molten alkali metal chlorides decreases with increasing molecular weight, and their temperature coefficients are weakly negative.

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**KEY WORDS:** alkali halides; forced Rayleigh scattering method; molten salts; thermal conductivity; thermal diffusivity.

## **1. INTRODUCTION**

Molten salts and their mixtures have been widely utilized as high-temperature heat transfer fluids, latent-heat thermal storage materials, and electrolytes for fuel cells because of their excellent thermal and chemical characteristics under high-temperature conditions. For the reliable thermal design of these systems, it is essential to obtain accurate thermophysical properties data on molten salts. However, in the case of thermal conduc-

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tivity and thermal diffusivity, there have been a very limited number of experimental studies, with discrepancies often far beyond their claimed accuracies. It seems quite difficult to make a judgment of the reliability of the available data since the experimental results vary by a factor of two to four. Moreover, we do not yet understand the temperature dependence of the thermal conductivity of molten salts, whether it is positive or negative.

This situation is due to the fact that the measurement of thermal conductivity and thermal diffusivity of molten salts is very difficult and complex because of their corrosiveness and high melting temperatures. Also, serious systematic errors are caused by radiative and convective heat transfer in the sample salt, which is inevitable when using the conventional steady-state methods. In the case of molten  $\text{NaNO}_3$  and  $\text{KNO}_3$ , it has been revealed by measurements using the transient hot-wire method with ceramic-coated probes [1, 2] that most of the previous data obtained by the steady-state methods contain significant systematic errors due to radiation and convection. However, the coated-wire technique cannot be extended to temperatures higher than about  $500^\circ\text{C}$ .

In order to solve the problem, we have developed the forced Rayleigh scattering method to measure the thermal diffusivity of molten salts up to about 1500 K. To date, we have developed a new apparatus for the measurement of normal liquids and liquid crystals [3, 4], analyzed error factors [5–7], and applied the method to high-temperature molten salts [8–10].

In the present series of studies, we extend our forced Rayleigh scattering measurements to molten alkali halides because of the following reasons: (1) they are useful materials for energy-related engineering applications, (2) they are suitable substances as standard reference materials for the thermal conductivity of fluids above 1000 K, and (3) they have the simplest molecular structure among other molten salts, which simplifies the theoretical assessment of experimental results. As the first paper in this series, we report the thermal diffusivity measurements of five molten alkali metal chlorides,  $\text{LiCl}$ ,  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{RbCl}$ , and  $\text{CsCl}$ , in the temperature range from 960 to 1440 K.

## 2. PRINCIPLE OF MEASUREMENTS AND EXPERIMENTAL APPARATUS

The present thermal diffusivity measurements have been based on the forced Rayleigh scattering method. Using this optical technique, the thermal diffusivity can be determined in a contact-free manner within the time interval of 1 ms, with a small temperature rise of 0.1 K and with a sample volume of about  $10\text{ mm}^3$ . Since the principle and error analysis

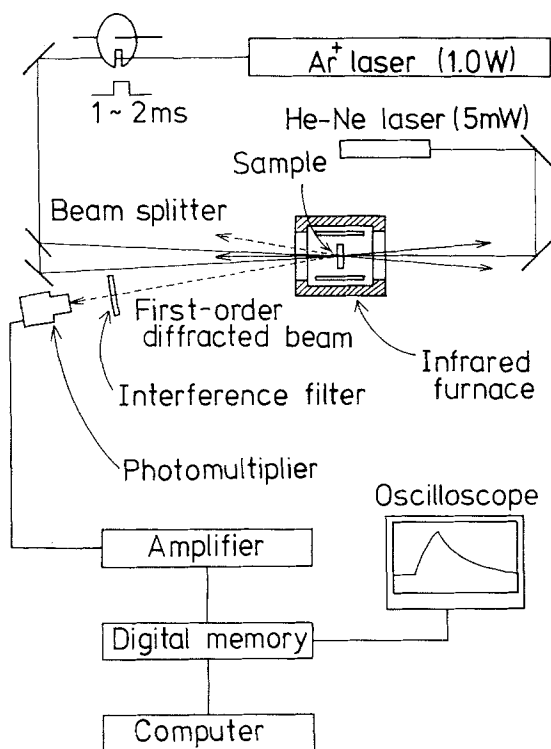


Fig. 1. Experimental apparatus (incident angle of probing laser beam is changed to zero).

appropriate to forced Rayleigh scattering measurements are described by Nagasaka et al. [5], in this paper we limit ourselves mainly to describing the experimental apparatus modified for the measurement of molten salts.

Figure 1 shows the present experimental apparatus. The heating laser is a single-mode argon-ion laser (wavelength = 514.5 nm, 1.0 W) and its continuous light is chopped by a rotating mechanical chopper to generate a short pulse of about 1 ms. The beam of the heating laser is divided into two beams of equal intensity by means of a beam splitter; the two beams cross in the sample to create the interference pattern. The sample is colored by the addition of a small amount of dye so that the sample can suitably absorb the energy of the heating laser beam. Consequently, the interference pattern induces a corresponding spatially sinusoidal temperature distribution, which acts as an optical phase grating for a low-power probing laser beam of nonabsorbed wavelength in the sample (He-Ne laser; wavelength = 632.8 nm, 5 mW). After short-pulse heating, the excited tem-

perature distribution decays exponentially by the heat conduction process in the sample. According to theory [5], we are able to choose the grating period  $A$ , sample thickness  $d$ , and absorption coefficient  $\alpha$  so that the assumption of one-dimensional heat conduction in the  $x$  direction is permissible. The decaying temperature profile, therefore, can be expressed by

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

where  $T$  is the temperature,  $t$  the elapsed time after the heating process,  $T_0$  the initial temperature,  $\Delta T_0$  the initial spatial temperature amplitude, and  $q = 2\pi/A$  the wave number of the interference pattern. Adopting the theory of diffraction, the intensity of the first-order diffracted probing beam  $I_1$  decays as

$$I_1 \propto \exp(-2t/\tau) \quad (2)$$

where  $\tau$  is the relaxation time constant of heat conduction in the sample. The thermal diffusivity of sample  $a$  is expressed using  $\tau$  and the grating period  $A$  by the following equation:

$$a = (1/\tau)(A/2\pi)^2 \quad (3)$$

Therefore, we can determine the thermal diffusivity by detecting the temporal decay of the first-order diffracted beam using a photomultiplier and by measuring the grating period.

It should be mentioned here that the incident angle of the probing laser beam is adjusted to zero (perpendicular to the sample surface) in the present experimental configuration. As pointed out by Nagasaka et al. [5], by setting an incident angle close to zero, the diffraction efficiency can be significantly improved. Actually, in comparison with the previously employed incident angle of  $2.25^\circ$ , the diffraction efficiency has been enhanced to about 12 times, which considerably improved the signal-to-noise ratio of  $I_1$  [9].

Figure 2 illustrates the sample cell made of quartz glass (1 mm in thickness) together with a cell holder. The surface of the glass cell walls is painted by a high-emissivity coating, excluding the laser beam spot area in order to secure enough absorption of infrared light from an infrared furnace shown in Fig. 1. The amount of sample needed for this type of cell is only 0.2 to 0.3 g. The temperature of the sample is measured with the aid of a ceramic-coated thermocouple (Type R) directly immersed in the sample. The accuracy of the temperature measured in this manner is estimated to be about  $\pm 15$  K, which is not so inferior if one considers the rather

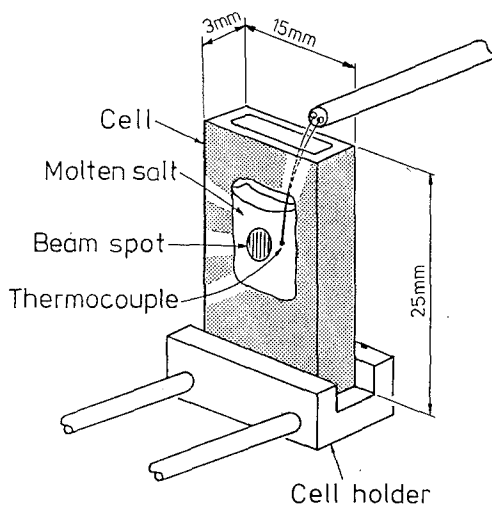


Fig. 2. Sample cell for molten salts.

weak temperature dependence of the thermal diffusivity of molten salts. In addition, the grating period is measured by means of a CCD image sensor within an accuracy of  $\pm 0.5\%$  [5].

The analysis of the recorded voltage change  $V(t)$ , which is proportional to  $I_1$ , is performed by Eq. (4) taking into account the coherent and the incoherent scattered light superimposed over the diffracted signal [5].

$$V(t) - V(\infty) = A \exp(-2t/\tau) + B \exp(-t/\tau) \quad (4)$$

with

$$B \ll 2 \sqrt{AV(\infty)} \cos \varphi \quad (5)$$

where  $A$  and  $B$  are the amplitude factors for the diffracted and the scattered light signals, respectively,  $V(\infty)$  is the measured background voltage shift, and  $\varphi$  is the phase difference between the diffracted signal and the coherent scattered light. In the actual procedure,  $V(t)$  data are fitted to Eq. (4) with the condition of Eq. (5) by the nonlinear least-square calculation.

### 3. RESULTS AND DISCUSSION

The experimental data for molten LiCl, NaCl, KCl, RbCl, and CsCl are listed in Tables I to V, respectively. Each sample used had a stated purity of not less than 99%. In these measurements, the grating period selected was about  $80 \mu\text{m}$ , depending on the measured substances, and the

**Table I.** Experimental Results for Thermal Diffusivity and Derived Thermal Conductivity of Molten LiCl

| $T$<br>(K) | $a$<br>[( $\text{m}^2 \cdot \text{s}^{-1}$ ) $\times 10^{-7}$ ] | $\lambda$<br>( $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ ) <sup>a</sup> |
|------------|---|--|
| 967        | 2.63  | 0.567  |
| 980        | 3.04  | 0.652  |
| 980        | 2.63  | 0.564  |
| 980        | 2.61  | 0.559  |
| 980        | 2.68  | 0.575  |
| 1003       | 2.73  | 0.581  |
| 1005       | 2.61  | 0.555  |
| 1006       | 2.91  | 0.621  |
| 1010       | 2.75  | 0.586  |
| 1125       | 2.97  | 0.611  |
| 1125       | 2.92  | 0.599  |
| 1126       | 2.92  | 0.599  |
| 1126       | 2.89  | 0.593  |
| 1212       | 2.50  | 0.501  |
| 1243       | 2.92  | 0.579  |
| 1245       | 2.13  | 0.422  |
| 1276       | 2.41  | 0.472  |
| 1279       | 2.73  | 0.535  |
| 1279       | 2.89  | 0.565  |
| 1283       | 2.29  | 0.448  |
| 1321       | 2.36  | 0.455  |

<sup>a</sup> For  $\lambda$  calculation,  $\rho$  ( $\text{kg} \cdot \text{m}^{-3}$ ) =  $1884.2 - 0.4328T$  (K) [12];  $C_p$  ( $\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$ ) = 1471.0 [13].

heating pulse duration time of the argon-ion laser was 1.2 ms. To color the transparent molten alkali halides, we found through many trial-and-error experiments that  $\text{K}_2\text{Cr}_2\text{O}_7$  is a more appropriate dye substance in terms of coloring ability and chemical stability at high temperatures than the previously used  $\text{CoCl}_2$  and  $\text{NiCl}_2$  [9]. The dye concentration was 1 wt% (about 2 to 3 mg) except in the case of LiCl (2.5 wt%). The effect of admixture of dye on the measured data is discussed later. The judgment of accuracy for the present thermal diffusivity measurements is similar to that described in Ref. 5. Taking into account the following error factors—the measurement of grating period, the determination of  $\tau$ , the imperfection of the one-dimensional heat conduction in the heated area, and the effect of scattered light—the overall accuracy of thermal diffusivity is estimated to be  $\pm 11\%$  for LiCl,  $\pm 4\%$  for NaCl,  $\pm 5\%$  for KCl,  $\pm 6\%$  for RbCl, and  $\pm 9\%$  for CsCl.

**Table II.** Experimental Results for Thermal Diffusivity and Derived Thermal Conductivity of Molten NaCl

| $T$<br>(K) | $a$<br>[ $(\text{m}^2 \cdot \text{s}^{-1}) \times 10^{-7}$ ] | $\lambda$<br>( $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ ) <sup>a</sup> |
|------------|--|--|
| 1170       | 2.80   | 0.497  |
| 1171       | 2.77   | 0.492  |
| 1172       | 2.82   | 0.501  |
| 1172       | 2.85   | 0.505  |
| 1172       | 2.77   | 0.492  |
| 1275       | 2.87   | 0.491  |
| 1286       | 2.90   | 0.493  |
| 1286       | 2.82   | 0.480  |
| 1287       | 2.77   | 0.472  |
| 1295       | 2.77   | 0.470  |
| 1297       | 2.77   | 0.470  |
| 1297       | 2.85   | 0.482  |
| 1353       | 2.82   | 0.468  |
| 1353       | 2.85   | 0.472  |
| 1354       | 2.82   | 0.468  |
| 1394       | 2.85   | 0.464  |
| 1398       | 2.82   | 0.460  |
| 1400       | 2.75   | 0.448  |
| 1399       | 2.82   | 0.460  |
| 1401       | 2.85   | 0.463  |
| 1401       | 2.82   | 0.459  |
| 1401       | 2.77   | 0.451  |
| 1402       | 2.87   | 0.467  |
| 1402       | 2.80   | 0.455  |
| 1436       | 2.77   | 0.445  |
| 1436       | 2.73   | 0.438  |
| 1437       | 2.77   | 0.445  |
| 1439       | 2.85   | 0.456  |
| 1439       | 2.87   | 0.461  |
| 1439       | 2.82   | 0.453  |
| 1439       | 2.82   | 0.453  |
| 1439       | 2.77   | 0.445  |
| 1439       | 2.77   | 0.445  |
| 1441       | 2.87   | 0.460  |

<sup>a</sup> For  $\lambda$  calculation,  $\rho$  ( $\text{kg} \cdot \text{m}^{-3}$ ) =  $2139.3 - 0.5430T$  (K) [12];  $C_p$  ( $\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$ ) = 1181 [14].

**Table III.** Experimental Results for Thermal Diffusivity and Derived Thermal Conductivity of Molten KCl

| $T$<br>(K) | $a$<br>[ $(\text{m}^2 \cdot \text{s}^{-1}) \times 10^{-7}$ ] | $\lambda$<br>$(\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1})^a$ |
|------------|--|---|
| 1056       | 2.61   | 0.389   |
| 1057       | 2.53   | 0.378   |
| 1057       | 2.57   | 0.383   |
| 1057       | 2.59   | 0.386   |
| 1058       | 2.42   | 0.362   |
| 1091       | 2.50   | 0.369   |
| 1091       | 2.59   | 0.382   |
| 1091       | 2.44   | 0.360   |
| 1091       | 2.64   | 0.389   |
| 1104       | 2.63   | 0.385   |
| 1104       | 2.55   | 0.374   |
| 1106       | 2.61   | 0.382   |
| 1106       | 2.63   | 0.385   |
| 1108       | 2.63   | 0.384   |
| 1150       | 2.53   | 0.364   |
| 1151       | 2.46   | 0.354   |
| 1152       | 2.44   | 0.351   |
| 1152       | 2.40   | 0.345   |
| 1155       | 2.40   | 0.345   |
| 1158       | 2.61   | 0.374   |
| 1159       | 2.55   | 0.366   |
| 1160       | 2.55   | 0.366   |
| 1161       | 2.48   | 0.355   |
| 1162       | 2.41   | 0.345   |
| 1189       | 2.57   | 0.364   |
| 1190       | 2.61   | 0.369   |
| 1190       | 2.59   | 0.366   |
| 1191       | 2.53   | 0.358   |
| 1192       | 2.53   | 0.358   |
| 1196       | 2.59   | 0.366   |
| 1197       | 2.53   | 0.357   |
| 1198       | 2.57   | 0.363   |
| 1198       | 2.69   | 0.380   |
| 1199       | 2.53   | 0.357   |
| 1245       | 2.42   | 0.335   |
| 1245       | 2.50   | 0.347   |
| 1246       | 2.29   | 0.317   |
| 1247       | 2.57   | 0.356   |
| 1249       | 2.46   | 0.340   |
| 1289       | 2.62   | 0.356   |
| 1291       | 2.57   | 0.349   |
| 1291       | 2.62   | 0.355   |
| 1297       | 2.69   | 0.364   |
| 1331       | 2.44   | 0.326   |
| 1335       | 2.32   | 0.310   |

<sup>a</sup> For  $\lambda$  calculation,  $\rho$  ( $\text{kg} \cdot \text{m}^{-3}$ ) =  $2136.0 - 0.5831T$  (K) [12];  $C_p$  ( $\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$ ) = 982.1 [14].



**Table IV.** Experimental Results for Thermal Diffusivity and Derived Thermal Conductivity of Molten RbCl

| $T$<br>(K) | $a$<br>[ $(\text{m}^2 \cdot \text{s}^{-1}) \times 10^{-7}$ ] | $\lambda$<br>( $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ ) <sup>a</sup> |
|------------|--|--|
| 1046       | 1.82   | 0.242  |
| 1046       | 1.84   | 0.245  |
| 1046       | 1.80   | 0.240  |
| 1046       | 1.82   | 0.242  |
| 1046       | 1.82   | 0.242  |
| 1119       | 1.79   | 0.231  |
| 1121       | 1.84   | 0.238  |
| 1123       | 1.84   | 0.237  |
| 1125       | 1.85   | 0.239  |
| 1126       | 1.84   | 0.237  |
| 1129       | 1.81   | 0.233  |
| 1129       | 1.78   | 0.229  |
| 1130       | 1.82   | 0.234  |
| 1130       | 1.73   | 0.223  |
| 1170       | 1.79   | 0.227  |
| 1173       | 1.70   | 0.216  |
| 1174       | 1.84   | 0.232  |
| 1175       | 1.87   | 0.236  |
| 1181       | 1.85   | 0.233  |
| 1242       | 1.80   | 0.221  |
| 1242       | 1.80   | 0.221  |
| 1243       | 1.82   | 0.223  |
| 1245       | 1.79   | 0.219  |
| 1247       | 1.81   | 0.222  |
| 1272       | 1.78   | 0.216  |
| 1275       | 1.77   | 0.214  |
| 1282       | 1.87   | 0.226  |
| 1282       | 1.94   | 0.235  |
| 1284       | 1.87   | 0.225  |
| 1289       | 1.73   | 0.208  |
| 1289       | 1.77   | 0.213  |
| 1289       | 1.72   | 0.207  |
| 1290       | 1.77   | 0.213  |
| 1291       | 1.85   | 0.222  |
| 1314       | 2.04   | 0.243  |
| 1317       | 1.63   | 0.194  |
| 1323       | 1.77   | 0.210  |
| 1325       | 1.84   | 0.218  |
| 1326       | 1.79   | 0.212  |
| 1326       | 1.69   | 0.200  |
| 1326       | 1.74   | 0.206  |
| 1351       | 1.74   | 0.204  |
| 1355       | 1.83   | 0.213  |

Table IV. (Continued)

| $T$<br>(K) | $a$<br>[(m <sup>2</sup> ·s <sup>-1</sup> ) × 10 <sup>-7</sup> ] | $\lambda$<br>(W·m <sup>-1</sup> ·K <sup>-1</sup> ) <sup>a</sup> |
|------------|---|---|
| 1357       | 1.88  | 0.219   |
| 1357       | 1.83  | 0.213   |
| 1358       | 1.82  | 0.212   |
| 1363       | 1.91  | 0.222   |
| 1410       | 1.99  | 0.227   |
| 1412       | 1.90  | 0.216   |
| 1414       | 1.64  | 0.186   |
| 1415       | 1.85  | 0.210   |
| 1416       | 1.77  | 0.201   |
| 1417       | 1.72  | 0.195   |
| 1418       | 1.74  | 0.197   |
| 1421       | 1.82  | 0.206   |
| 1422       | 1.67  | 0.189   |
| 1437       | 1.71  | 0.193   |
| 1441       | 1.65  | 0.186   |

<sup>a</sup> For  $\lambda$  calculation,  $\rho$  (kg·m<sup>-3</sup>) = 3121.1 - 0.8832*T* (K) [12];  $C_p$  (J·kg<sup>-1</sup>·K<sup>-1</sup>) = 607.6 [14].

Since no previous studies are available on the thermal diffusivity of these molten salts, we converted our thermal diffusivity data into thermal conductivity using carefully selected literature values of the density and the specific heat capacity. For the densities we used the correlations reported by Van Artsdalen and Yaffe [11] and Yaffe and Van Artsdalen [12], which are believed to be accurate within  $\pm 0.5\%$ . On the other hand, for specific heat capacity, unfortunately, adequately reliable data are scarce up to the present time. Consequently, we tentatively used the following temperature-independent values, with estimated accuracies less than those claimed by the authors:  $\pm 7$  to  $\pm 8\%$  for LiCl by Bockris and Richards [13],  $\pm 3$  to  $\pm 4\%$  for NaCl by Murgulescu and Telea [14],  $\pm 3$  to  $\pm 4\%$  for KCl by Murgulescu and Telea [14],  $\pm 7$  to  $\pm 8\%$  for RbCl by Murgulescu and Telea [14], and  $\pm 7$  to  $\pm 8\%$  for CsCl by Murgulescu and Telea [14].

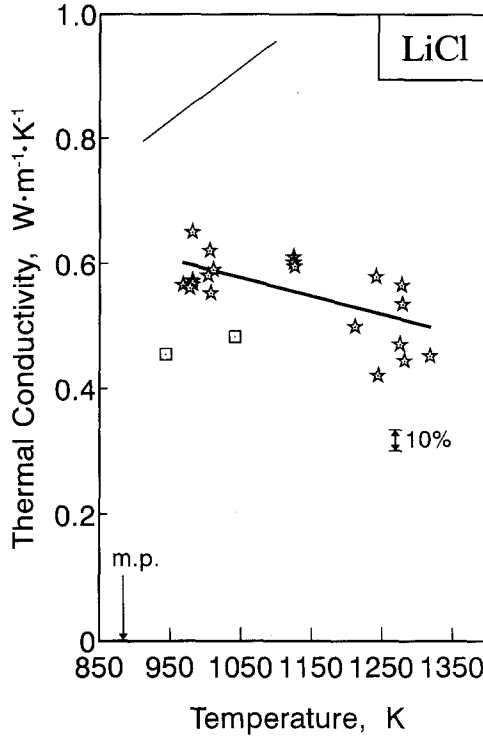
### 3.1. LiCl

Figure 3 shows the present thermal conductivity results for molten LiCl compared with earlier works. The accuracy of the converted thermal conductivity of molten LiCl is estimated to be  $\pm 20\%$ . Even near the

**Table V.** Experimental Results for Thermal Diffusivity and Derived Thermal Conductivity of Molten CsCl

| $T$<br>(K) | $\alpha$<br>[ $(\text{m}^2 \cdot \text{s}^{-1}) \times 10^{-7}$ ] | $\lambda$<br>( $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ ) <sup>a</sup> |
|------------|---|--|
| 960        | 1.64  | 0.202  |
| 961        | 1.61  | 0.199  |
| 961        | 1.64  | 0.203  |
| 961        | 1.64  | 0.203  |
| 961        | 1.62  | 0.200  |
| 992        | 1.65  | 0.202  |
| 993        | 1.64  | 0.201  |
| 994        | 1.66  | 0.203  |
| 994        | 1.70  | 0.207  |
| 995        | 1.70  | 0.207  |
| 1054       | 1.59  | 0.189  |
| 1132       | 1.56  | 0.181  |
| 1133       | 1.59  | 0.184  |
| 1134       | 1.57  | 0.181  |
| 1136       | 1.59  | 0.184  |
| 1238       | 1.60  | 0.177  |
| 1272       | 1.57  | 0.171  |
| 1272       | 1.53  | 0.166  |
| 1273       | 1.54  | 0.167  |
| 1274       | 1.54  | 0.167  |
| 1278       | 1.52  | 0.165  |
| 1289       | 1.56  | 0.168  |
| 1289       | 1.46  | 0.158  |
| 1290       | 1.54  | 0.166  |
| 1290       | 1.47  | 0.158  |
| 1290       | 1.59  | 0.172  |
| 1303       | 1.26  | 0.135  |
| 1304       | 1.76  | 0.189  |
| 1304       | 1.64  | 0.175  |
| 1305       | 1.64  | 0.176  |
| 1305       | 1.65  | 0.177  |
| 1336       | 1.44  | 0.152  |
| 1360       | 1.44  | 0.151  |

<sup>a</sup> For  $\lambda$  calculation,  $\rho$  ( $\text{kg} \cdot \text{m}^{-3}$ ) =  $3769.1 - 1.0650T$  (K) [12];  $C_p$  ( $\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$ ) =  $450.5$  [14].

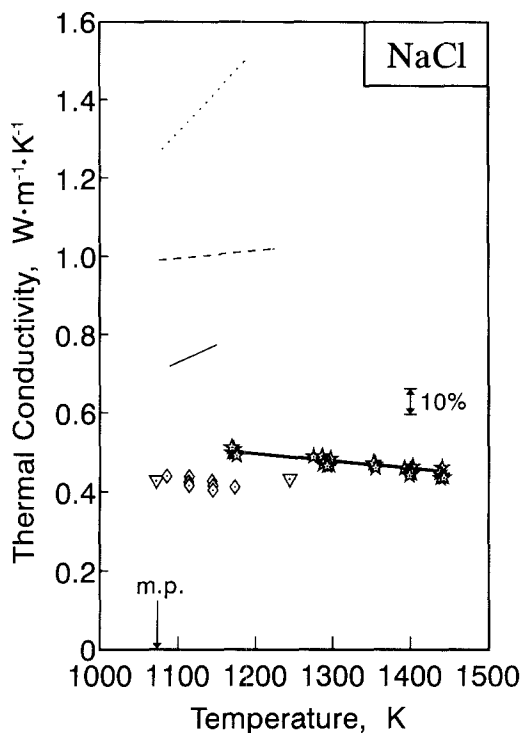


**Fig. 3.** Thermal conductivity of molten LiCl:  $\square$ , McDonald and Davis [16]; —, Smirnov et al. [15];  $\star$ , present work. The present thermal diffusivity data were used to obtain thermal conductivity.

melting point, our results exhibit rather large scattering. The reason is that during the course of measurements, the quartz glass cell turned slightly opaque (devitrification phenomena), which significantly increased the scattered light of the probing laser in the detected light signals. Such an increase in scattered light signals decreases the reproducibility. At the present time, this sort of difficulty seems hard to solve, especially for fluorides like LiF and KF. It is worth mentioning that even a sapphire glass is corroded completely by these fluoride salts. The data of Smirnov et al. [15] measured by the steady-state concentric cylinder method are larger than ours, with a maximum deviation of about 60%, and have a positive temperature dependence. The results of McDonald and Davis [16], obtained with the transient hot-wire method using a U-shape platinum wire sheathed with a quartz tube, agree with the present results within the claimed accuracy.

### 3.2. NaCl

The present results for molten NaCl are compared with those of previous works in Fig. 4. In contrast with LiCl, the reproducibility of the measurement is reasonable, within  $\pm 2.6\%$ . The accuracy of the converted thermal conductivity is estimated to be  $\pm 8\%$ . The previous thermal conductivity values of molten NaCl scatter from about  $0.4$  to  $1.5 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  and their temperature coefficients are positive values. In contrast, the present results are some of the lowest of all and agree well with the data of Golyshev et al. [17] obtained by the steady-state concentric cylinder method (molybdenum wall; gap, 1 mm) with radiation error correction and with the data of Harada [18] measured by the modified



**Fig. 4.** Thermal conductivity of molten NaCl: ---, Fedorov and Machuev [22]; ····, Bystrai et al. [21];  $\nabla$ , Golyshev et al. [17]; —, Smirnov et al. [15];  $\diamond$ , Harada [18];  $\star$ , present work. The present thermal diffusivity data were used to obtain thermal conductivity.

laser flash method [19, 20]. Moreover, the present temperature dependence of the thermal conductivity exhibits a weak negativity. The data of Bystrai et al. [21] measured by the necked down sample method are almost 300% larger than ours. It is thus considered that all these data are influenced strongly by the convection and radiation heat losses, all of which increase the apparent thermal conductivity. This conclusion is appropriate for all other molten salts measured in the present study.

### 3.3. KCl

Figure 5 displays the present results for molten KCl including comparisons with other experimental data. We remeasured this salt, since we have changed the incident angle of the probing beam in order to gain

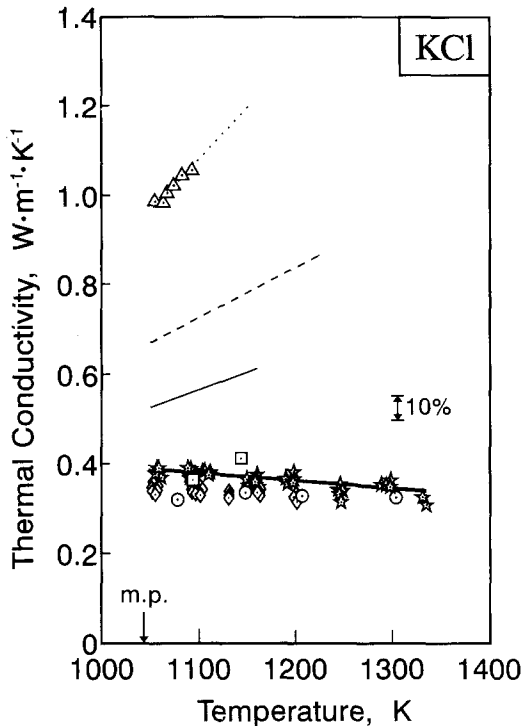


Fig. 5. Thermal conductivity of molten KCl: ---, Fedorov and Machuev [22];  $\square$ , McDonald and Davis [16];  $\triangle$ , Polyakov and Gil'debrandt [23];  $\cdots$ , Bystrai et al. [21]; —, Smirnov et al. [15];  $\circ$ , Hatakeyama et al. [8];  $\diamond$ , Harada [18];  $\star$ , present work. The present thermal diffusivity data were used to obtain thermal conductivity.

a better signal-to-noise ratio. Furthermore, we have discovered that  $K_2Cr_2O_7$  is more suitable as a dye substance in comparison with the previously used  $NiCl_2$  and  $CoCl_2$  [8, 9]. As a result, the present data have a better reproducibility and accuracy than obtained in the previous study. The converted thermal conductivity results have an estimated accuracy of  $\pm 8\%$ . Comparing the previously reported data of Smirnov et al. [15], Fedorov and Machuev [22], and Polyakov and Gil'debrandt [23], all obtained by the steady-state concentric cylinder method, with the present results, again we can identify that all these data are strongly affected with the systematic error due to radiation and convection. On the other hand, the data of McDonald and Davis [16] (transient hot-wire method using a quartz-coated U-tube), Harada [18] (modified laser flash method), and Hatakeyama et al. [8] measured by the same method as used in the present study, coincide with the present results.

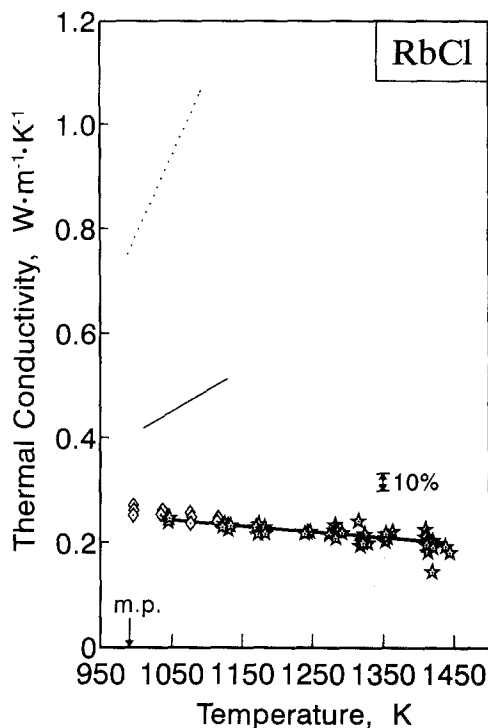


Fig. 6. Thermal conductivity of molten RbCl:  $\cdots$ , Bystrai et al. [24];  $—$ , Smirnov et al. [15];  $\diamond$ , Harada [18];  $\star$ , present work. The present thermal diffusivity data were used to obtain thermal conductivity.

### 3.4. RbCl

The present thermal conductivity results for molten RbCl are compared with those of previous works in Fig. 6. The overall accuracy of the converted thermal conductivity is estimated to be  $\pm 15\%$ . Again, the data of Bystrai et al. [24] and Smirnov et al. [15] are far higher than ours. Bystrai et al. [24] employed the necked down sample method, which is based on measurement of the steady-state change in resistance caused by electrical heating of a narrow bridge of the sample material joined to two larger volumes of the same material. It should be mentioned that this method is quite questionable when applied to molten salts. On the contrary, data of Harada [18] coincide quite well with ours.

### 3.5. CsCl

Figure 7 shows the thermal conductivity results for molten CsCl with analogous comparison with the case of molten RbCl. The differences

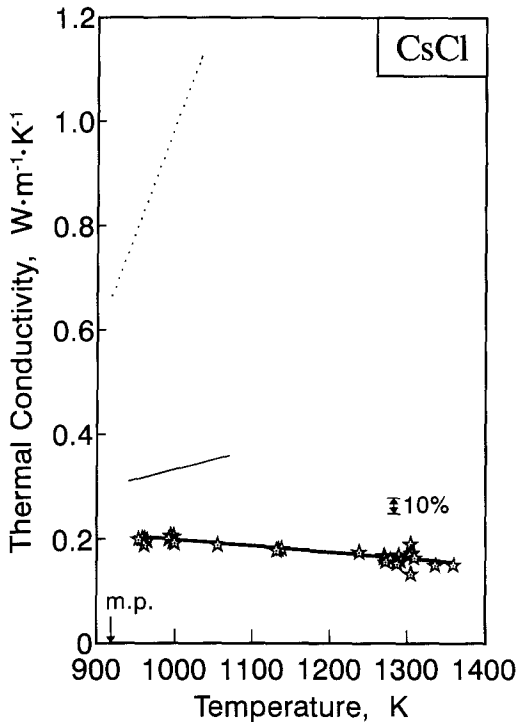


Fig. 7. Thermal conductivity of molten CsCl: ····, Bystrai et al. [24]; —, Smirnov et al. [15]; ☆, present work. The present thermal diffusivity data were used to obtain thermal conductivity.



Table VI. Optimum Values of the Coefficients in Eq. (6)

|      | $\lambda_m$<br>( $W \cdot m^{-1} \cdot K^{-1}$ ) | $b$<br>[( $W \cdot m^{-1} \cdot K^{-2}$ ) $\times 10^{-4}$ ] | $T_m$<br>(K) | Temperature range<br>(K) |
|------|--|--|--------------|--------------------------|
| LiCl | 0.626  | -2.9   | 883          | 967-1321                 |
| NaCl | 0.519  | -1.8   | 1074         | 1170-1441                |
| KCl  | 0.389  | -1.7   | 1043         | 1056-1335                |
| RbCl | 0.249  | -1.1   | 990          | 1046-1441                |
| CsCl | 0.209  | -1.2   | 918          | 960-1360                 |

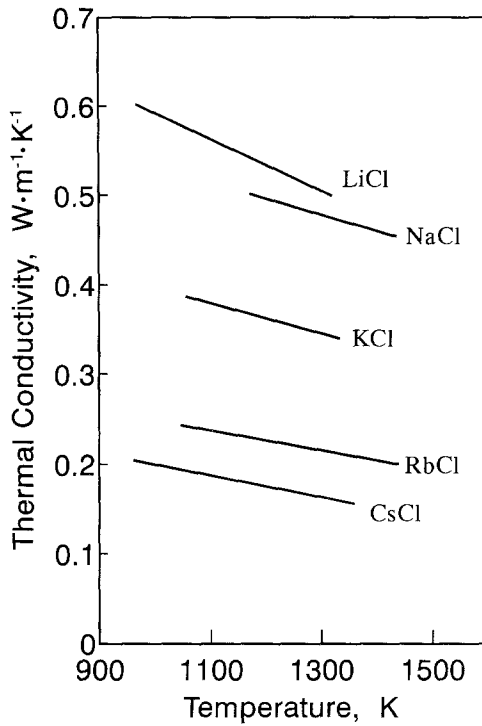


Fig. 8. Thermal conductivity of molten alkali metal chlorides calculated by Eq. (6).

reach about 550%, at the maximum. At temperatures above 1300 K, the scattering of our data became slightly larger. This may be due to the devitrification phenomenon as described in Section 3.1. The estimated accuracy of the converted thermal conductivity is  $\pm 18\%$ .

### 3.6. Summary of the Thermal Conductivity of Molten Alkali Metal Chlorides

The thermal conductivities of molten alkali metal chlorides studied in this paper vary with temperature according to the following empirical linear equation.

$$\lambda = \lambda_m + b(T - T_m) \quad (6)$$

The values of  $\lambda_m$  and  $b$  calculated from the present experimental data by least-squares fitting are given in Table VI. These correlated results are presented in Fig. 8. As can be seen from these summarized results, the thermal conductivity of molten alkali metal chlorides decreases with increasing molecular weight. Besides, the temperature coefficients are all weakly negative and the slope becomes slightly steeper with decreasing molecular weight.

## 4. EFFECT OF DYE CONCENTRATION

In this method, suitable absorption of the heating laser beam has to be produced by the admixture of a dye. The addition of dye introduces two kinds of error sources: (1) the changes in thermophysical properties and (2) the nonuniform initial temperature distribution in the direction of sample thickness due to the strong absorption coefficient. The second problem has already been dealt with analytically by Nagasaka et al. [5]. The first can be confirmed only through experimental verification, even though the concentration of dye should be kept low enough not to have any detectable influence on the thermophysical properties of the sample. To perform this verification for molten salts, we have chosen molten NaCl as a reference sample by adding  $K_2Cr_2O_7$  as a dye substance at three percentages: 0.5, 1.0, and 2.5 wt%. As shown in Fig. 9, although the results of a 2.5% admixture of dye tend to be measured slightly lower, the agreement of these results is well within the estimated accuracy of  $\pm 8\%$ . Since in the actual measurements we used a 1 wt% concentration of dye, it is possible to conclude that the effect of dye concentration on thermal conductivity is insignificant in the present study.

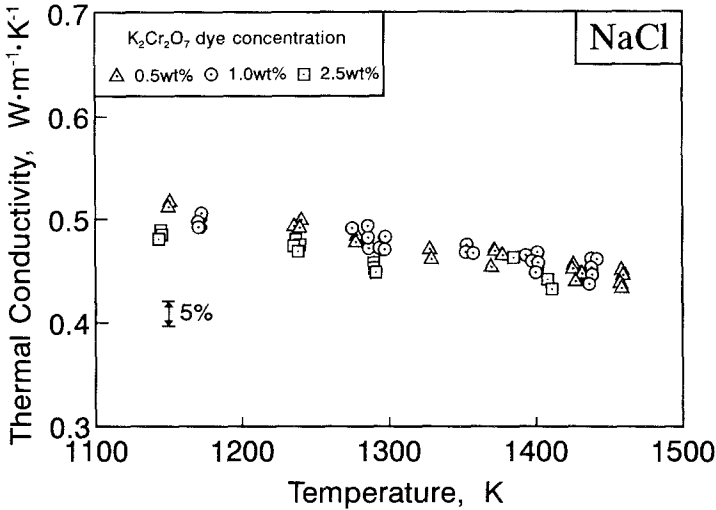


Fig. 9. Effect of dye concentration on the measured thermal conductivity of molten NaCl.

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