Experimental Determination of the Thermal Diffusivity of Molten Alkali Halides by the Forced Rayleigh Scattering Method. II. Molten NaBr, KBr, RbBr, and CsBr

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This is a companion to an earlier paper (on molten alkali metal chlorides) which gives experimental results for the thermal diffusivity of four molten alkali metal bromides: NaBr, KBr, RbBr, and CsBr. The measurements were performed with a forced Rayleigh scattering instrument at temperatures up to 1326 K. The overall uncertainty in the measured thermal diffusivity is estimated to be ± 3 to ± 11 %, depending on the measured salts. The results converted to thermal conductivity show one of the smallest values among other earlier experimental data obtained mainly by the steady-state methods. It is also found that the temperature dependence of the thermal conductivity is weakly negative.

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

1. INTRODUCTION

In a previous paper [1], measurements of the thermal diffusivity of molten alkali metal chlorides, LiCl, NaCl, KCl, RbCl, and CsCl, were described. The instrument based on the forced Rayleigh scattering methods permits the measurements of the thermal diffusivity of molten salts at temperatures up to 1440 K with an estimated accuracy of ± 4 to ± 11 %. In this paper, measurements of the thermal diffusivity of NaBr, KBr, RbBr, and CsBr are reported. The temperature ranges studied were 948 to 1326 K. The overall accuracy of the reported values is estimated to be ± 3 to ± 11 %.

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Т (К)	$a [(m^2 \cdot s^{-1}) \times 10^{-7}]$	$(\mathbf{W}\cdot\mathbf{m}^{-1}\cdot\mathbf{K}^{-1})^a$
1050	2.10	0.318
1051	1.98	0.300
1051	2.04	0.309
1051	2.18	0.330
1107	2.03	0.300
1109	2.08	0.309
1109	2.20	0.326
1109	2.21	0.328
1109	2.18	0.323
1110	2.27	0.336
1110	2.07	0.307
1111	2.15	0.318
1111	2.07	0.307
1111	2.07	0.307
1163	2.30	0.335
1163	2.07	0.301
1164	2.07	0.301
1164	2.23	0.324
1165	2.18	0.317
1165	2.27	0.329
1165	2.08	0.303
1105	2,04	0.290
1105	2.03	0.294
1100	2.04	0.290
1209	2.04	0.292
1210	2.01	0.287
1211	2.00	0.205
1211	2.23	0.300
1211	2.10	0.307
1212	2.08	0.298
1212	2.00	0.291
1213	2.08	0.298
1214	2.15	0.306
1261	2.07	0.290
1264	2.04	0.286
1265	2.10	0.294
1265	2.15	0.300
1265	2.05	0.287
1265	2.16	0.303
1266	2.16	0.303
1266	2.16	0.303
1266	2.21	0.310
1267	2.08	0.291

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

^{*a*} For λ calculation, ρ (kg·m⁻³)=3174.9-0.8169T (K) [5] and C_p (J·kg⁻¹·K⁻¹)=653.3 [6].

Т (К)	$a [(m^2 \cdot s^{-1}) \times 10^{-7}]$	$\lambda (\mathbf{W} \cdot \mathbf{m}^{-1} \cdot \mathbf{K}^{-1})^a$	
1035	1.76	0.216	
1036	1.77	0.217	
1036	1.75	0.215	
1036	1.78	0.218	
1036	1.75	0.214	
1086	1.80	0.216	
1088	1.79	0.215	
1088	1.78	0.214	
1090	1.83	0.220	
1092	1.76	0.211	
1150	1.83	0.214	
1152	1.84	0.215	
1152	1.81	0.212	
1152	1.82	0.213	
1153	1.82	0.213	
1196	1.82	0.209	
1196	1.80	0.207	
1197	1.88	0.215	
1197	1.84	0.211	
1198	1.83	0.210	
1243	1.78	0.201	
1244	1.86	0.209	
1244	1.84	0.207	
1245	1.86	0.208	

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

^a For λ calculation, ρ (kg·m⁻³) = 2958.7 - 0.8253T (K) [5] and C_p (J·kg⁻¹·K⁻¹) = 581.8 [6].

2. EXPERIMENTAL

The thermal diffusivity measurements were performed with the forced Rayleigh scattering instrument described in detail elsewhere [2–4]. The experimental procedure and the method used for the evaluation of the data remained the same as in our earlier work [1]. The samples of NaBr, KBr, RbBr, and CsBr had a nominal purity of better than 99%. All measurements were performed at atmospheric pressure.

3. RESULTS AND DISCUSSION

Tables I to IV list the experimental data for thermal diffusivity and derived thermal conductivity of molten NaBr, KBr, RbBr, and CsBr,

Т (К)	$a [(m^2 \cdot s^{-1}) \times 10^{-7}]$	$\frac{\lambda}{(\mathbf{W}\cdot\mathbf{m}^{-1}\cdot\mathbf{K}^{-1})^a}$
1031	1.76	0.204
1031	1.72	0.199
1032	1.67	0.194
1033	1.67	0.194
1033	1.56	0.181
1102	1.65	0.186
1103	1.65	0.186
1104	1.61	0.182
1105	1.68	0.189
1107	1.66	0.187
1176	1.67	0.182
1177	1.65	0.180
1177	1.67	0.182
1178	1.73	0.188
1179	1.66	0.181
1256	1.70	0.179
1258	1.64	0.172
1259	1.66	0.175
1260	1 59	0.167
1261	1.60	0.168
1320	1.62	0.166
1322	1.67	0.171
1324	1.67	0.171
1325	1.57	0.160
1326	1.50	0.153

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

^{*a*} For λ calculation, ρ (kg·m⁻³) = 3739.2-1.0718*T* (K) [5] and C_p (J·kg⁻¹·K⁻¹) = 440.2 [6].

respectively. The overall accuracy of thermal diffusivity is estimated to be $\pm 7\%$ for NaBr, $\pm 3\%$ for KBr, $\pm 7\%$ for RbBr, and $\pm 11\%$ for CsBr based on the assessment described in Ref. 1.

To our knowledge, no other measurements of the thermal diffusivity of these molten salts exist; therefore, for comparison we converted our results into thermal conductivity using carefully selected literature values of density and specific heat capacity. For the densities, we employed the correlations by Yaffe and Van Artsdalen [5], which are believed to be accurate within $\pm 0.5\%$. For specific heat capacity, we employed the following constant values with estimated uncertainties larger than those claimed by Murgulescu and Telea [6]: ± 7 to $\pm 8\%$ for NaBr, ± 3 to $\pm 4\%$ for KBr, ± 7 to $\pm 8\%$ for RbBr, and ± 7 to $\pm 8\%$ for CsBr.

Т (К)	$a [(m^2 \cdot s^{-1}) \times 10^{-7}]$	$(\mathbf{W}\cdot\mathbf{m}^{-1}\cdot\mathbf{K}^{-1})^a$
948	1.32	0.149
950	1.34	0.152
950	1.42	0.160
950	1.40	0.158
950	1.33	0.150
1029	1.25	0.137
1032	1.28	0.140
1034	1.32	0.144
1039	1.27	0.138
1039	1.30	0.141
1120	1.27	0.134
1120	1.22	0.128
1121	1.29	0.135
1124	1.24	0.130
1125	1.29	0.135
1193	1.38	0.141
1194	1.22	0.125
1196	1.26	0.128
1196	1.52	0.155
1197	1.49	0.151
1252	1.44	0.143
1256	1.41	0.140
1312	1.52	0.147
1312	1.69	0.163
1314	1.48	0.143

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

^{*a*} For λ calculation, ρ (kg·m⁻³)=4245.1-1.2234*T* (K) [5] and C_p (J·kg⁻¹·K⁻¹)=366.1 [6].

3.1. NaBr

In Fig. 1, the present thermal conductivity results for molten NaBr are presented. In the same figure measurements of other investigators are also included. The measurements of McDonald and Davis [7], performed by a transient hot-wire method using a U-shaped platinum wire sheatled with a quartz tube with an accuracy of $\pm 10\%$, coincide with the present thermal conductivity results with an estimated accuracy of $\pm 15\%$. Also, the data by Harada [8], measured with a modified laser flash method [9, 10], agree well with the present results. On the other hand, the data of Smirnov et al. [11], obtained with a steady-state concentric cylinder method with a



Fig. 1. Thermal conductivity of molten NaBr: ⊡ McDonald and Davis [7]; ◇ Harada [8]; (—) Smirnov et al. [11]; ☆ present work. The present thermal diffusivity data were used to obtain thermal conductivity.

claimed accuracy of $\pm 4\%$, differ by about 150 to 180% from our data. We conclude that this significant disagreement may be attributed to the systematic error caused by radiation and convection heat losses in the steady-state measurements, which become serious with increasing temperature.

3.2. KBr

Figure 2 displays the present results for molten KBr including comparisons with other experimental data. In this case, the results of Harada [8] agree well with the present results, however, two experimental data of McDonald and Davis [7] are about 40% larger than ours (estimated accuracy of $\pm 7\%$).



Fig. 2. Thermal conductivity of molten KBr: \Box McDonald and Davis [7]; \diamond Harada [8]; (—) Smirnov et al. [11]; \Rightarrow present work. The present thermal diffusivity data were used to obtain thermal conductivity.

3.3. RbBr

The present thermal conductivity results for molten RbBr are compared with those of earlier works in Fig. 3. Again, the measurements of Harada, performed by a modified laser flash method, agree with ours, whereas the data of Smirnov et al. [11], measured with the steady-state concentric-cylinder method, are far larger than ours.

3.4. CsBr

The only other measurements are those performed by Smirnov et al. [11] with a concentric-cylinder instrument with a claimed uncertainty of $\pm 4\%$. As shown in Fig. 4, the deviation of these measurements from our results is more than 200%.



Fig. 3. Thermal conductivity of molten RbBr: \diamond Harada [8]; (—) Smirnov et al. [11]; \Rightarrow present work. The present thermal diffusivity data were used to obtain thermal conductivity.

3.5. Summary of the Thermal Conductivity of Molten Alkali Metal Bromides

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

$$\lambda = \lambda_{\rm m} + b(T - T_{\rm m}) \tag{1}$$

The values of λ_m and b calculated from the present experimental data by least-squares fitting are given in Table V; T_m is the melting point. These correlated results are presented in Fig. 5. As can be seen from these summarized results, the thermal conductivity of molten alkali metal bromides decreases with increasing molecular weight. The temperature coefficients of thermal conductivity are all weakly negative.



Fig. 4. Thermal conductivity of molten CsBr: (-) Smirnov et al. [11]; \Rightarrow present work. The present thermal diffusivity data were used to obtain thermal conductivity.

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	$(\mathbf{W} \cdot \mathbf{m}^{-1} \cdot \mathbf{K}^{-1})$	$b = [(\mathbf{W} \cdot \mathbf{m}^{-1} \cdot \mathbf{K}^{-2}) \times 10^{-4}]$	T _m (K)	Temperature range (K)
NaBr	0.320	-0.8	1020	1050-1267
KBr	0.218	-0.4	1007	1035-1245
RbBr	0.203	-1.1	953	1031-1326
CsBr	0.149	-0.2	909	948-1314

Table V. Optimum Values of the Coefficients in Eq. (1)



Fig. 5. Thermal conductivity of molten alkali metal bromides calculated by Eq. (1).

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