Reference Correlations for the Thermal Conductivity of 13 Inorganic Molten Salts

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Reference Correlations for the Thermal Conductivity of 13 Inorganic Molten Salts

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The available experimental data for the thermal conductivity of 13 inorganic molten salts have been critically examined with the intention of establishing thermal conductivity reference correlations. All experimental data have been categorized into primary and secondary data according to the quality of measurement specified by a series of criteria. Standard reference correlations are proposed for the following molten salts (with estimated uncertainties at the 95% confidence level given in parentheses): $LiNO_3$ (7%), $NaNO_3$ (7%), KNO_3 (15%), NaBr (15%), KBr (15%), RbBr (15%), LiCl (17%), NaCl (20%), KCl (17%), RbCl (17%), CsCl (10%), NaI (17%), and RbI (20%). https://doi.org/10.1063/1.5052343

Key words: molten salts; reference correlation; thermal conductivity.

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1. Introduction

In most modern commercial Concentrating Solar Power (CSP) plants, molten salt mixtures composed of two nitrates (commercial name Solar Salt)[b] or three nitrates (commercial name HITEC) are usually utilized as the heat transfer or storage medium.[1] Molten salt mixtures are also employed in Molten Salt Nuclear Reactors (MSNR)[2] as the heat transfer fluid. Notwithstanding this use of molten salts, their thermal conductivity is not well established even for single species, which is surprising given the importance of this property in heat transfer. The need for reference correlations for even the pure molten salts can be easily demonstrated if one examines, for example, Fig. 1, where the results of all available measurements[3–10] for the thermal conductivity of molten NaCl are shown as a function of the temperature at atmospheric pressure. As shown in Fig. 1, at temperatures near 1175 K, the results from different authors range from 400 to 1500 W m^{-1} K^{-1}. In the same figure, the reference equation proposed by Janz *et al.*[11] in 1979 is also shown. It is obvious that the situation requires an appraisal.

In 1979, Janz *et al.*[11] proposed reference correlations for the thermal conductivity of some molten salts. However, as there were only a limited number of measurements at that time, these correlations should be re-examined today. In 1991, Nagasaka and Nagashima[12] proposed reference correlations for the thermal conductivity of molten KNO_3 and $NaNO_3$. They critically examined all available measurements and proposed correlations based upon the measurements of Kitade *et al.*[13] All these earlier work will be carefully examined in this paper.

In 2016, following an established need for reference values for the thermal conductivity of molten metals, a project was initiated by the International Association for Transport Properties, IATP (formerly the Subcommittee on Transport Properties of the International Union of Pure and Applied Chemistry, IUPAC) to critically evaluate all available measurements and propose reference correlations as a function of the temperature at atmospheric pressure. Thus, reference correlations for molten copper, gallium, indium, iron, lead, nickel, and tin were proposed,[14] and subsequently expressions were proposed for molten bismuth, cobalt, germanium, and silicon.[15] The present work extends this investigation to the thermal conductivity of a series of molten inorganic salts. All available measurements of molten nitrate, bromide, chloride, and iodide salts of Group I metals were examined. For 13 of them ($LiNO_3$, $NaNO_3$, KNO_3, NaBr, KBr, RbBr, LiCl, NaCl, KCl, RbCl, CsCl, NaI, and RbI), sufficient measurements of acceptable quality exist so that reference correlations can be proposed.

2. Experimental Techniques

The analysis described here is applied to the best available experimental data for the thermal conductivity of the molten salts. Thus, a prerequisite to the analysis is a critical

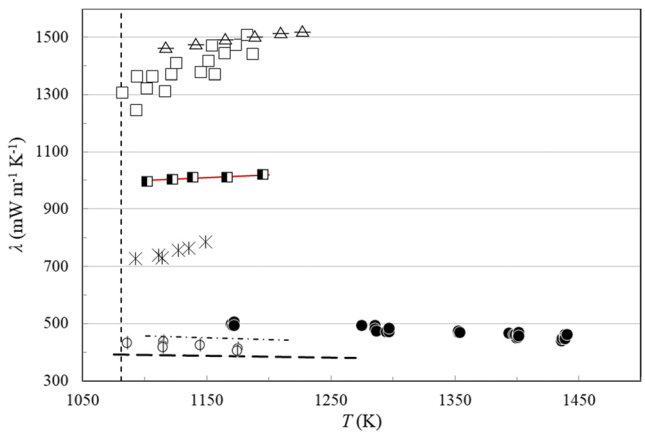

FIG. 1. Thermal conductivity at 0.1 MPa of molten NaCl as a function of the temperature. Golyshev and Gonik[3] (— —), Nagasaka *et al.*[4] (●), Smirnov *et al.*[5] (✱), Harada *et al.*[6] (ϕ), Bystrai and Dessyatnik[7] (□), Veneraki *et al.*[8] (—•), Egorov and Revyakina[9] (△), Fedorov and Matsuev[10] (◧), and the reference correlation of Janz *et al.*[11] (red line); melting point temperature (- -).

[b]Commercial equipment, instruments, or materials are identified only in order to adequately specify certain procedures. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products identified are necessarily the best available for the purpose.

assessment of the experimental data. For this purpose, two categories of experimental data are defined: primary data, employed in the development of the correlation, and secondary data, used simply for comparison purposes. According to the recommendation adopted by IATP, the primary data are identified by a well-established set of criteria (such as availability of a complete working equation, low-uncertainty measured principal variables, description of purification methods, etc.).[16] These criteria have been successfully employed to establish standard reference values for the viscosity and thermal conductivity of fluids over wide ranges of conditions, with uncertainties in the range of 1%. However, in many cases, such a narrow definition unacceptably limits the thermodynamic states for which data can be represented. Consequently, within the primary data set, it is also necessary to include results that extend over a wide range of conditions, albeit with a poorer accuracy, provided they are consistent with other more accurate data or with theory. In all cases, the accuracy claimed for the final recommended data must reflect the estimated uncertainty in the primary information.

Molten salts of Group I metals are highly reactive at high temperature. Hence, it is difficult to find an appropriate container for the salts during the measurement of thermophysical properties. Moreover, convection induced by a non-uniform temperature field in molten salts at high temperatures is exceedingly difficult to avoid completely so that the measurement of thermal conductivity is generally contaminated by convective flows of heat, as well as radiative heat losses.

A large number of techniques have been employed for the determination of the thermal conductivity of these materials, namely, forced-Rayleigh scattering, concentric cylinders, laser flash, transient hot wire, parallel plates, and other techniques. These will be discussed in Subsections 2.1–2.6.

It should finally be mentioned that some techniques, like forced-Rayleigh scattering, concentric cylinders, and laser flash, actually measure the thermal diffusivity. To obtain the thermal conductivity, knowledge of the heat capacity and the density of the salt is required. In most cases, the investigators themselves also publish thermal conductivity values; otherwise, the conversion to thermal conductivity is discussed in the text.

2.1. Forced Rayleigh scattering technique

The beam of a heating laser is divided into two beams of equal intensity by a beam splitter; the two beams cross in the sample to create an 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 a non-absorbed wavelength in the sample. After short-pulse heating, the excited temperature distribution decays exponentially by the heat conduction process in the sample. The thermal diffusivity is detected by observing the temporal decay of the first-order diffracted beam using a photomultiplier and by measuring the grating wavelength. The technique was developed by the group headed by Professor Nagasaka and is backed by a full theory and an uncertainty analysis of all parameters involved. The effect of other heat transfer mechanisms is shown to be minimal while, in particular, convection would be directly observable. It has successfully been employed for the measurement of selected chloride,[4,17] bromide,[18] and iodide salts.[19] All of these measurements were considered primary data.

2.2. Concentric-cylinders technique

The melt is placed in the space between two concentric cylinders. The thermal conductivity is obtained from the steady-state temperature gradient across the melt, when a measured rate of heat is generated in the inner cylinder, if the process is one of pure radial conduction. However, the configuration of the instrument means that there is inevitably heat transport by convection in a gravitational field and heat transport between the surfaces by radiation. The effect of the former mechanism depends on the thickness of the melt layer and the latter on the emissivity of the cylinder walls. These factors all tend to increase the rate of heat transfer if they occur and become larger as the measurement temperature increases. Golyshev and Gonik[3] showed that the radiation contribution could give rise to an erroneous positive temperature dependence, the slope of which was a function of the emissivity of the walls of the container. Thus, if an investigator had problems with convection and radiation, these effects were likely to worsen with temperature, T, and possibly result in a positive temperature coefficient $(\partial\lambda/\partial T)|_p$ for the thermal conductivity, λ, at constant temperature. They also investigated the effect of the melt layer thickness and indicated that small thicknesses reduced the effects of convection.

Golyshev and Gonik[3] employed a melt layer of 1 mm thickness to suppress convection and cylinders of 200 mm height, made of molybdenum. Molybdenum has a low emissivity, and the authors claimed a negligible contribution of the emittance of cell walls to the heat transfer, even at high temperatures. Extra care was taken to minimize heat losses. Uncertainty of 5%–6% was quoted. These measurements were considered as primary data.

To minimize the exchange of heat by convection and the corrections related to the radiation-conduction coupling, Tufeu *et al.*[20] employed a very small gap of 0.2 mm. The internal cylinder was 120 mm in length and 20 mm in diameter, while the external cylinder was 50 mm in external diameter and 200 mm in length. Silver was used as the cylinder material, and the surfaces in contact with the sample were polished and their emissivity was estimated to be as low as 0.02. The uncertainty of the measurements was estimated to be better than 4%. Over the temperature range of their experiments, they concluded that the thermal conductivity of molten KNO_3 and $NaNO_3$ is temperature independent. These measurements were also part of the primary data.

We also included in the primary data set the measurements of Veneraki *et al.*[8] because they examined the effect of

different gap sizes (1.37–2.19 mm), the effect of the graphite cells, and the effect of the absorption coefficient. The uncertainty of these measurements is quoted as 8%.

The measurements of White and Davis[21] show a positive temperature dependence, which is probably attributed to convection arising in the large gap (3.18 mm) between the cylinders. Furthermore, conduction heat losses were up to 30% of the total heat supplied. A large gap was also employed by McDonald and Davis[22] (2.54 mm). In this case, the apparatus operated in a relative mode. They discussed problems of heat loss associated with their previous instrument[21] and attempted to re-measure the thermal conductivity of those melts, but their measurements were not very consistent. Both these sets were not considered part of the primary data.

A large gap (3 mm) was also employed by Fedorov and Machuev[10] and Polyakov and Gildebrandt.[23] Both these sets were found to be affected by convection and radiation effects, increasing with higher measurement temperature. Similar behavior is observed in the measurements of Savintsev *et al.*[24] and Egorev and Revyakina,[9] who employed a 2 mm and 3 mm gap, respectively. However, their measurements were affected by considerable axial heat loss because of problems associated with achieving temperature equilibrium. Bloom *et al.*[25] employed a very small gap (0.9 mm). However their measurements also seem to be affected by convection and radiation, increasing with measurement temperature, most probably associated with temperature equilibrium. Finally, a large positive temperature dependence of the thermal conductivity of the melt is also observed in the results of Smirnov *et al.*[5] They employed a small gap (1.2 mm), but the results are several times higher (a factor of two in most cases) than the data of all other investigators. This is probably attributed to high heat losses from the top and bottom of their vessel, as can be seen from the instrument design,[5] which departs dramatically from the carefully designed equivalent instrument of Tufeu *et al.*[20] All these measurements were also not included in the primary data set.

2.3. Laser flash technique

Harada *et al.*[6] in 1992 employed two kinds of laser flash methods for three-layered systems (metal disk/sample liquid/metal disk) in order to measure the thermal conductivity of molten salts. One is to measure the temperature response at the front surface of the upper metal disk below which a sample liquid layer was located, and the other is to measure the temperature response at the rear surface of the lower metal disk above which the sample liquid and the upper metal disk layers are present. The effect of radiation on the temperature response was explicitly taken into account. The thermal conductivities obtained by the two methods agreed with each other within the experimental precision, and the reproducibility of the data was within 10%. Thermal conductivities measured showed a weak negative temperature dependence. These measurements were included as part of the primary data set.

The technique of heating with a laser the front surface of the upper metal disk was also employed by Ohta *et al.*[26] They observed a slight increase in thermal conductivity with an increase of the sample thickness, attributed to an uncorrected heat leak to the side wall of the cell. Furthermore, a positive temperature dependence is apparent, indicating the influence of heat loss. Hence this set was not included in the primary data set. An *et al.*[27] also employed the laser flash technique, but they also observed heat losses attributed to a heat leak to the side of the cell. Furthermore, their two measurements also show an increasing thermal conductivity with temperature, indicating the strong influence of unaccounted-for heat loss. Hence this set was not included in the primary data set.

2.4. Transient hot-wire technique

Kitade *et al.*[13] employed the transient hot-wire technique with ceramic-coated probes, consisting of a 30 μm diameter Pt wire insulated by a 4 μm thick layer of Al_2O_3 (produced by ion plating). Very short measuring times were employed, and the effect of radiation was calculated to be negligible. The uncertainty was claimed to be 3%, and the results obtained from different probes agreed well with each other within the estimated uncertainty. Omotani *et al.*[28,29] employed a modified transient hot-wire method with liquid metal (mercury) in a capillary as a heat source. The capillary was made of quartz glass with an outer diameter of about 90 μm, an inner diameter of 45 μm, and a length of 100 mm. The apparatus was operated in a relative mode calibrated against toluene. They claimed to have succeeded in eliminating errors due to convection. The uncertainty of the measurement is claimed to be 3%. Both these sets were part of the primary data set.

Having employed the concentric-cylinders technique, McDonald and Davis[30] attempted to perform measurements with the transient hot-wire technique employing a thick 101 μm diameter Pt wire in a quartz tube. Although they avoided radiation, their measurements were strongly affected by convection and thus were much higher than other reliable measurements and furthermore showed a strong positive increase with temperature. Finally, an insulated wire was also employed by Zhang and Fujii.[31] They employed a short thick Pt wire of 9.2 mm length and 97 μm diameter, welded at both ends to thick Pt lead wires. The sensor was coated by sputtering with Al_2O_3 to create a 2 μm thickness insulating film and calibrated with water and toluene. These measurements also showed a positive increase with temperature. Both of these sets were not included in the primary data set.

The transient hot-wire technique was employed by three more investigators: Turnbull,[32] McLaughlin,[33] and Powell *et al.*[34] However, these experiments employed a bare wire and were conducted before the development of the full theory of the transient hot wire.[35,36] Hence, their measurements suffer from leakage currents, as well as convective effects, and were not included in the primary data set.

2.5. Parallel-plates technique

Santini *et al.*[37] employed the relative parallel-plate method with heat flowing downward. The heat flux was measured by a ''fluxmeter'' under which there exists thermal bond material and molten salt. The instrument was calibrated with silicone

oil. There was no description of the gap employed. Although this steady-state method is suitable for solid materials, its application to high-temperature molten salts inevitably introduces considerable systematic errors due to heat losses. A similar instrument was employed by Araki *et al.*,[38] who improved the original instrument developed by Kato *et al.*[39] Although a more systematic theoretical analysis was carried out, their measurements were still higher than those considered as primary data and thus were not included in the primary data set. Tye *et al.*[40] also employed this technique. However,

TABLE 1. Data sets considered for the thermal conductivity of molten nitrate salts at 0.1 MPa

First author	Publication year	Purity[a] (mass %)	Technique employed[b]	Uncertainty quoted (%)	No. of data	Temperature range (K)	Form of data[c]
			$LiNO_3$				
Previous reference correlation							
Janz[11]	1979	...	(Based on McDonald[22])	20	...	530–730	E
Primary data							
Asahina[41]	1988	...	Pulse-heated flat plate (TD)	4	6	536–588	D
Omotani[29]	1984	...	Transient hot wire (liquid probe)	3	3	531–568	T
Secondary data							
Araki[38]	1983	...	Parallel plates (TD)	...	4	539–603	D
Tye[40]	1977	99.80	Parallel plates (TD)	...	6	533–623	T
McDonald[22]	1970	...	Concentric cylinders (2.54 mm)	5	...	553–728	E
Gustaffson[43]	1968	Anal	Transient plane source	10	7	532–581	T
White[21]	1967	...	Concentric cylinders (3.18 mm)	3	...	553–648	E
			$NaNO_3$				
Previous reference correlation							
Nagasaka[12]	1991	...	(Based on Kitade[13])	5	...	584–662	E
Janz[11]	1979	...	(Based on McDonald[22])	20	...	590–740	E
Primary data							
Kitade[13]	1989	99.00	Transient hot wire (insulated)	3	28	583–661	T
Asahina[41]	1988	...	Pulse-heated flat plate (TD)	4	5	583–651	D
Tufeu[20]	1985	...	Concentric cylinders (0.2 mm)	4	10	593–673	T
Omotani[28]	1982	99.90	Transient hot wire (liquid probe)	3	1	587.7	T
Odawara[44]	1977	...	Wave-front interferometer (TD)	...	9	581–691	T
Secondary data							
Zhang[31]	2000	99.95	Transient hot wire (insulated)	3	3	603–664	T
Ohta[26]	1990	...	Laser flash (TD)	...	8	592–660	D
Santini[37]	1983	...	Parallel plates (TD)	...	...	583–651	E
Kato[38]	1977	...	Parallel plates (TD)	4.5	10	595–654	D
McDonald[22]	1970	...	Concentric cylinders (2.54 mm)	5	...	593–728	E
Gustafsson[42]	1968	Anal	Transient plane source	2.6	9	588–727	T
White[21]	1967	...	Concentric cylinders (3.18 mm)	5	5	619–692	D
Bloom[25]	1965	Anal	Concentric cylinders (0.9 mm)	5	6	602–695	T
			KNO_3				
Previous reference correlation							
Nagasaka[12]	1991	...	(Based on Kitade[13])	5	...	622–712	E
Janz[11]	1979	...	(Based on McDonald[22])	20	...	610–730	E
Primary data							
Kitade[13]	1989	99.00	Transient hot wire (insulated)	3	22	621–710	T
Asahina[41]	1988	...	Pulse-heated flat plate (TD)	4	5	618–656	D
Harada[45]	1985	99.50	Laser flash (TD)	10	4	688–702	D
Tufeu[20]	1985	99.99	Concentric cylinders (0.2 mm)	4	5	617–700	T
Secondary data							
An[27]	2015	...	Laser flash (TD)	...	2	623–633	T
Ohta[26]	1990	...	Laser flash (TD)	...	9	621–694	D
Araki[38]	1983	...	Parallel plates (TD)	...	9	616–741	D
Santini[37]	1983	...	Parallel plate (TD)	...	6	627–768	D
Powell[34]	1979	...	Transient hot wire	10	...	623–723	E
McDonald[22]	1970	...	Concentric cylinders (2.54 mm)	5	16	610–734	D
Gustafsson[42]	1968	Anal	Transient plane source	2.6	8	611–724	T
White[21]	1967	...	Concentric cylinders (3.18 mm)	5	6	615–704	D
Bloom[25]	1965	Anal	Concentric cylinders (0.9 mm)	5	4	616–666	T
McLaughlin[33]	1964	...	Transient hot wire	...	1	683	T
Turnbull[32]	1961	...	Transient hot wire	3	7	608–667	D

[a]Anal = Analytic grade.
[b]TD = thermal diffusivity measurement.
[c]D = diagram, E = equation, and T = tabulated experimental data.

their values were shown to increase with temperature and were much higher than all others. Hence they were not included in the primary data set.

2.6. Other techniques

Asahina *et al.*[41] employed the pulse-heated flat plate technique. This is a transient technique where a thin metal plate is pulse-heated electrically for a short period (less than 1 s). The thermal diffusivity is calculated as a function of the pulse time from the temperature rise detected with a thin thermocouple placed at some distance below the metal plate, in the sample liquid. The thermal diffusivities of the salts were found to almost be independent of temperature over the temperature range of their measurements. These measurements were included in the primary data set.

Gustaffson *et al.*[42,43] measured the thermal conductivity by the non-steady-state optical interferometric technique (transient plane source technique). The plane source was realized by using an electrically heated metal foil suspended in the liquid. The temperature distribution is described by employing instantaneous heat sources giving a simple expression of the optical path, which is recorded with wave-front-shearing interferometry. The measurements were completed within 10 s. Errors due to radiation were considered to be negligible. The uncertainty was claimed to be 2.6% for the thermal conductivity. The investigators did not consider the effect of current leakage from the bare metallic metal foil heat source to the molten salt. This set was not included in the primary data set. Odawara *et al.*,[44] however, modified the technique of Gustaffson *et al.*,[43] employing wave-front-shearing interferometry, and the thermal conductivity was calculated from the temperature dependence of the determined refractive index. They also performed a study of convective effects. Their measurements showed a negative dependence on temperature as temperature increased. This set was included in the primary data set.

Finally, the data of Bystrai and Desyatnik[7] measured by the necked-down sample method are almost 300% larger than other primary data. It is thus considered that all these data are influenced strongly by convection and radiation heat losses, all of which increase the apparent thermal conductivity. This set was not included among the primary data.

3. Data Compilation

Tables 1–4 present the data sets found for the measurement of the thermal conductivity of some molten nitrate salts (KNO_3, $LiNO_3$, $NaNO_3$), bromide salts (KBr, NaBr, RbBr), chloride salts (CsCl, KCl, LiCl, NaCl, RbCl), and iodide salts (NaI, RbI). In these tables, the purity of the sample, the technique employed, and the uncertainty quoted are also presented. Furthermore, the form in which the data are presented and the temperature range covered are also noted. As already discussed in Sec. 2, the data sets have been classified into primary and secondary sets, according to the discussion of each technique in Sec. 2.

4. Discussion

The primary data for the thermal conductivity λ (mW m^{-1} K^{-1}) are shown in Tables 1–4 for each molten salt. For each fluid, the data were fitted as a function of the absolute temperature, T (K), to a linear equation of the form

TABLE 2. Data sets considered for the thermal conductivity of molten bromide salts at 0.1 MPa

First author	Publication year	Purity (mass %)	Technique employed[a]	Uncertainty quoted (%)	No. of data	Temperature range (K)	Form of data[b]
			NaBr				
Primary data							
Harada[6]	1992	99.50	Laser flash (TD)	10	13	1031–1151	D
Nakazawa[18]	1992	99.00	Forced Rayleigh scattering (TD)	7	44	1050–1267	T
Secondary data							
Smirnov[5]	1987	...	Concentric cylinders (1.2 mm)	4	5	1044–1124	D
McDonald[30]	1971	...	Transient hot wire (insulated)	10	2	1075–1124	T
			KBr				
Primary data							
Harada[6]	1992	99.50	Laser flash (TD)	10	10	1020–1111	D
Nakazawa[18]	1992	99.00	Forced Rayleigh scattering (TD)	3	24	1035–1245	T
Secondary data							
Smirnov[5]	1987	...	Concentric cylinders (1.2 mm)	4	5	1024–1099	D
McDonald[30]	1971	...	Transient hot wire (insulated)	10	2	1061–1123	T
			RbBr				
Primary data							
Harada[6]	1992	99.50	Laser flash (TD)	10	7	984–1086	D
Nakazawa[18]	1992	99.00	Forced Rayleigh scattering (TD)	7	25	1031–1326	T
Secondary data							
Smirnov[5]	1987	...	Concentric sylinders (1.2 mm)	4	5	984–1075	D

[a]TD = thermal diffusivity measurement.
[b]D = diagram and T = tabulated experimental data.

TABLE 3. Data sets considered for the thermal conductivity of molten chloride salts at 0.1 MPa

First author	Publication year	Purity (mass %)	Technique employed[a]	Uncertainty quoted (%)	No. of data	Temperature range (K)	Form of data[b]
LiCl							
Previous reference correlation							
Janz[11]	1979	...	(Based on McDonald[30])	20	2	947–1047	T
Primary data							
Nagasaka[4]	1992	99.00	Forced Rayleigh scattering (TD)	11	21	967–1321	T
Secondary data							
Smirnov[5]	1987	...	Concentric cylinders (1.2 mm)	4	6	908–1088	D
Bystrai[7]	1975	...	Necked-down sample	10	10	922–1007	D
McDonald[30]	1971	...	Transient hot wire (insulated)	10	2	943–1043	T
NaCl							
Previous reference correlation							
Janz[11]	1979	...	(Based on Fedorov[10])	20	...	1100–1200	E
Primary data							
Golyshev[3]	1992	...	Concentric cylinders (1 mm)	5.5	...	1075–1270	E
Harada[6]	1992	99.50	Laser flash (TD)	10	7	1086–1175	D
Nagasaka[4]	1992	99.00	Forced Rayleigh scattering (TD)	4	34	1170–1441	T
Veneraki[8]	1976	...	Concentric cylinders (1.37–2.19 mm)	8	...	1100–1216	E
Secondary data							
Smirnov[5]	1987	...	Concentric cylinders (1.2 mm)	4	6	1092–1150	D
Bystrai[7]	1975	...	Necked-down sample	10	16	1081–1186	D
Egorov[9]	1972	...	Concentric cylinders (2–3 mm)	10	7	1090–1230	D
Fedorov[10]	1970	...	Concentric cylinders (3 mm)	10	5	1101–1196	D
KCl							
Previous reference correlation							
Janz[11]	1979	...	(Based on Fedorov[10] and Bystrai[7])	20	...	1050–1200	E
Primary data							
Golyshev[3]	1992	...	Concentric cylinders (1 mm)	6.3	...	1053–1253	E
Harada[6]	1992	99.50	Laser flash (TD)	10	14	1052–1198	D
Nagasaka[4]	1992	99.00	Forced Rayleigh scattering (TD)	5	45	1056–1335	T
Nagasaka[17]	1988	99.00	Forced Rayleigh scattering (TD)	7	19	1071–1303	D
Secondary data							
Smirnov[5]	1987	...	Concentric cylinders (1.2 mm)	4	5	1053–1159	D
Bystrai[7]	1975	...	Necked-down sample	10	12	1063–1162	D
Polyakov[23]	1974	...	Concentric cylinders (3 mm)	...	6	1055–1093	T
Egorov[9]	1972	...	Concentric cylinders (2–3 mm)	10	7	1053–1177	D
McDonald[30]	1971	...	Transient hot wire (insulated)	10	2	1093–1143	T
Fedorov[10]	1970	...	Concentric cylinders (3 mm)	10	5	1061–1190	D
RbCl							
Primary data							
Harada[6]	1992	99.50	Laser flash (TD)	10	7	997–1117	D
Nagasaka[4]	1992	99.00	Forced Rayleigh scattering (TD)	6	58	1046–1441	T
Secondary data							
Smirnov[5]	1987	...	Concentric cylinders (1.2 mm)	4	5	1016–1128	D
Bystrai[7]	1975	...	Necked-down sample	10	10	996–1085	D
CsCl							
Primary data							
Nagasaka[4]	1992	99.00	Forced Rayleigh scattering (TD)	9	33	960–1360	T
Secondary data							
Smirnov[5]	1987	...	Concentric cylinders (1.2 mm)	4	5	944–1063	D
Savintsev[24]	1978	...	Concentric cylinders (2 mm)	...	...	940–1070	E
Bystrai[7]	1975	...	Necked-down sample	10	13	923–1027	D

[a]TD = thermal diffusivity measurement.
[b]D = diagram, E = equation, and T = tabulated experimental data.

$$\lambda = c_0 + c_1(T - T_m), \quad (1)$$

where T_m (K) is the melting temperature of the salt,[46] and the coefficients c_0 (mW m^{-1} K^{-1}) and c_1 (mW m^{-1} K^{-2}) are given in Table 5. In the same table, the maximum temperature of applicability of Eq. (1), derived from the corresponding maximum temperatures in Tables 1–4, is also presented. Equation (1) is valid from the melting temperature up to this maximum temperature. We note that measurements were

TABLE 4. Data sets considered for the thermal conductivity of molten iodide salts at 0.1 MPa

First author	Publication year	Purity (mass %)	Technique employed[a]	Uncertainty quoted (%)	No. of data	Temperature range (K)	Form of data[b]
			NaI				
Primary data							
Harada[6]	1992	99.50	Laser flash (TD)	10	10	943–1104	D
Nakazawa[19]	1992	99.00	Forced Rayleigh scattering (TD)	7	11	961–1099	T
Secondary data							
Smirnov[5]	1987	...	Concentric cylinders (1.2 mm)	4	8	959–1079	D
McDonald[30]	1971	...	Transient hot wire (insulated)	10	2	978–1073	T
			RbI				
Primary data							
Harada[6]	1992	99.50	Laser flash (TD)	10	7	925–1006	D
Nakazawa[19]	1992	99.00	Forced Rayleigh scattering (TD)	6	31	963–1226	T
Secondary data							
Smirnov[5]	1987	...	Concentric cylinders (1.2 mm)	4	5	939–1092	D

[a]TD = thermal diffusivity measurement.
[b]D = diagram and T = tabulated experimental data.

weighted in the fitting process inversely proportional to their uncertainty squared.

In the same table, two more quantities are given. Percentage deviation for each salt is defined as $\left(\frac{100}{\lambda_{av}}\right)\sqrt{\left[\sum_n(\lambda_{exp}-\lambda_{fit})^2\right]/n}$, where λ_{exp}, λ_{fit}, and λ_{av} represent in turn the experimental thermal conductivity, experimental thermal conductivity fitted with Eq. (1), and the average thermal conductivity for the range examined, respectively, while n is the number of measurements. The percentage deviation characterizes the statistical goodness of the fit, but it can be, and usually is, much smaller than the quoted uncertainty of each measurement set. It is therefore not always a good measure of the uncertainty that should be ascribed to the correlated property. It becomes a less good measure as the number of measurements considered is statistically small and the investigators' quoted uncertainties are different. Hence, it was preferred to define one more quantity, the uncertainty of the thermal conductivity fitted by our equation—shown in the last column of Table 5. This uncertainty was not determined statistically but incorporates some subjective judgment based upon the claims of different authors. In making these estimates of uncertainty, we have been rather conservative, so we intend the uncertainty value we quote should correspond roughly to a 95% confidence level.

4.1. Nitrate molten salts

The primary data of the thermal conductivity of molten $LiNO_3$, $NaNO_3$, and KNO_3, shown in Table 1, are depicted in Fig. 2. We note that in order to convert the thermal diffusivity measurements of Asahina *et al.*[41] and Odawara *et al.*,[44] we employed literature values for the heat capacity[47] (uncertainty of 1.5%) and density[11] (uncertainty of 1%). The remaining investigators measured directly, or quoted in their papers, thermal-conductivity values.

In Fig. 2, in addition to the primary data, the reference correlation of Janz *et al.*[11] for the three molten salts and

TABLE 5. Coefficients of Eq. (1), melting temperatures, maximum temperature of application, and associated uncertainties

Molten salt	T_m (K)	T_{max} (K)	c_0 (mW m^{-1} K^{-1})	c_1 (mW m^{-1} K^{-2})	Deviation (%)	Uncertainty 2σ (%)
$LiNO_3$	527.15	588	572.6	−0.142	6.5	7
$NaNO_3$	583.15	691	519.1	−0.137	4.2	7
KNO_3	610.15	710	430.3	−0.422	10.1	15
NaBr	1020.15	1267	318.0	−0.085	7.1	15
KBr	1007.15	1245	227.4	−0.089	6.4	15
RbBr	953.15	1326	205.4	−0.110	5.6	15
LiCl	883.15	1321	628.1	−0.310	15.6	17
NaCl	1081.15	1441	475.5	−0.180	13.5	20
KCl	1045.15	1335	359.3	−0.085	12.0	17
RbCl	990.15	1441	253.8	−0.123	8.1	17
CsCl	918.15	1360	208.8	−0.115	9.3	10
NaI	935.15	1104	220.2	−0.037	12.0	17
RbI	913.15	1226	140.9	−0.106	9.6	20

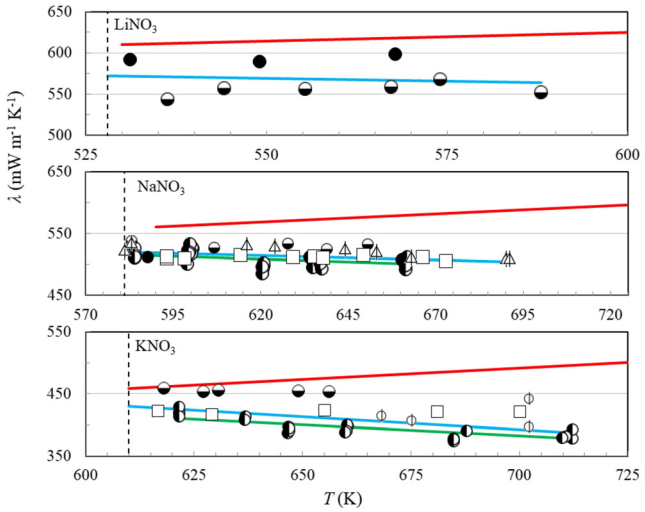

FIG. 2. Primary data and previous reference correlations for the thermal conductivity of $LiNO_3$, $NaNO_3$, and KNO_3 as a function of the temperature. Kitade *et al.*[13] (◐), Asahina *et al.*[41] (◒), Harada and Shioi[45] (Φ), Tufeu *et al.*[20] (□), Omotani and Nagashima[29] (●), Odawara[44] *et al.* (◭). Equation (1) (blue line) and previous reference correlations of Nagasaka and Nagashima[12] (green line) and Janz *et al.*[11] (red line); melting temperature. (- -).

the reference correlation proposed by Nagasaka and Nagashima[12] for KNO_3 and $NaNO_3$ are shown. Since the correlations proposed by Janz *et al.*[11] in 1979 were based on selected measurements that existed at that time, they are now considered to produce values that are too high.

The resulting reference correlations for the nitrate salts are in good agreement with the previous two reference correlations by Nagasaka and Nagashima.[12] In Fig. 3, the

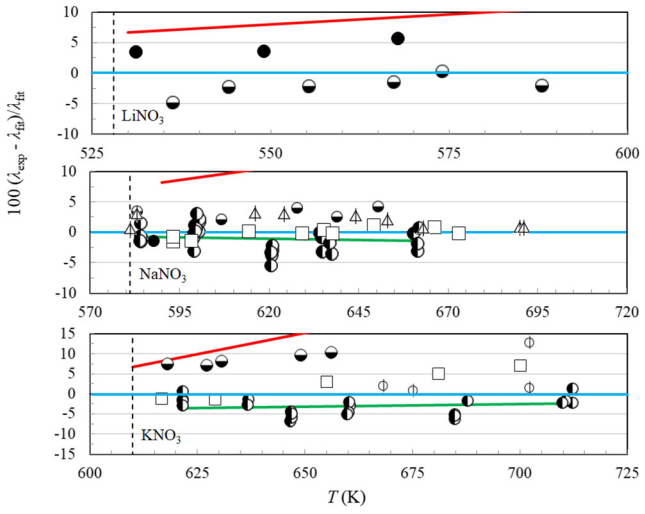

FIG. 3. Percentage deviations of the primary data and previous reference correlations for the thermal conductivity of $LiNO_3$, $NaNO_3$, and KNO_3 from the values produced by Eq. (1), as a function of the temperature. Kitade *et al.*[13] (◐), Asahina *et al.*[41] (◒), Harada and Shioi[45] (Φ), Tufeu *et al.*[20] (□), Omotani and Nagashima[29] (●), Odawara[44] *et al.* (◭), and reference correlations of Nagasaka and Nagashima[12] (green line) and Janz *et al.*[11] (red line). Melting temperature. (- -).

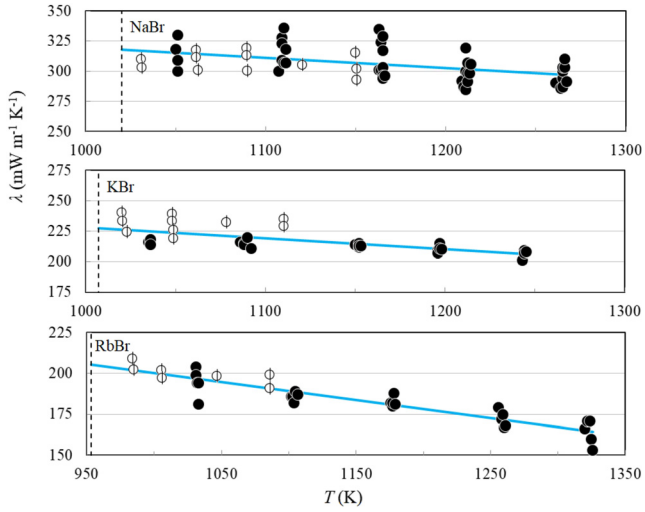

FIG. 4. Primary data for the thermal conductivity of NaBr, KBr, and RbBr as a function of the temperature. Harada *et al.*[6] (Φ), Nakazawa *et al.*[18] (●), and Eq. (1) (blue line); melting temperature (- -).

percentage deviations of the primary data from the values produced by Eq. (1) are shown as a function of the temperature.

4.2. Bromide molten salts

The primary data of the thermal conductivity of molten NaBr, KBr, and RbBr, shown in Table 2, are depicted in Fig. 4. In this case, following the discussion of Sec. 2, only two primary data sets (Harada *et al.*[6] and Nakazawa *et al.*[18]) are considered for each bromide salt. No previous reference correlation exists, to our knowledge. The data were correlated according to Eq. (1), and the coefficients, together with the uncertainty of each correlation, are shown in Table 5. Figure 5 shows the percentage deviations of the primary data from the

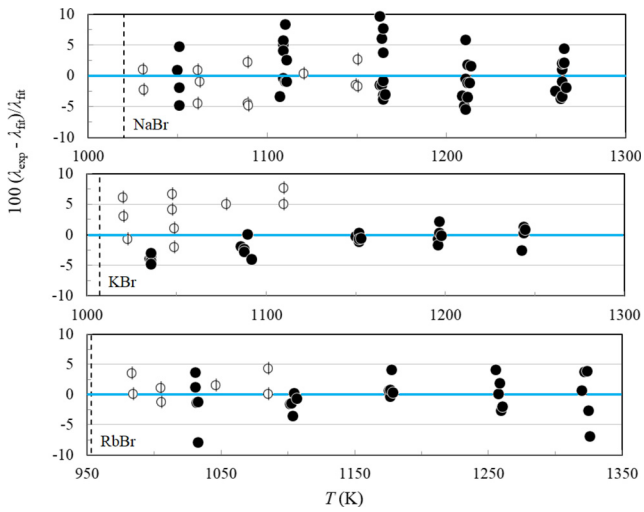

FIG. 5. Percentage deviations of the primary data for the thermal conductivity of NaBr, KBr, and RbBr from the values produced by Eq. (1), as a function of the temperature. Harada *et al.*[6] (Φ) and Nakazawa *et al.*[18] (●); melting temperature (- -).

values calculated by using Eq. (1) and the corresponding coefficients of Table 5.

4.3. Chloride molten salts

The primary data of the thermal conductivity of molten LiCl, NaCl, KCl, RbCl, and CsCl shown in Table 3 are depicted in Fig. 6. The following can be noted: (a) In the case of the thermal conductivity of molten CsCl and LiCl, following the discussion in Sec. 2, the measurements of only one investigator (Nagasaka *et al.*[4]) have been considered as primary data—see Table 3. Since, however, this particular group has produced excellent measurements for all other salts, consistent with other reliable measurements, trust can be placed in their results. (b) Janz *et al.*[11] proposed reference correlations for molten KCl, LiCl, and NaCl. However, as these were based on the measurements existing at that time, they are now considered too high—see, for example, Fig. 1.

In Fig. 7, the percentage deviations of the primary data for molten LiCl, NaCl, KCl, RbCl, and CsCl from the values produced by Eq. (1) are shown as a function of the temperature.

4.4. Iodide molten salts

Finally, the primary data of the thermal conductivity of molten NaI and RbI shown in Table 4 are depicted

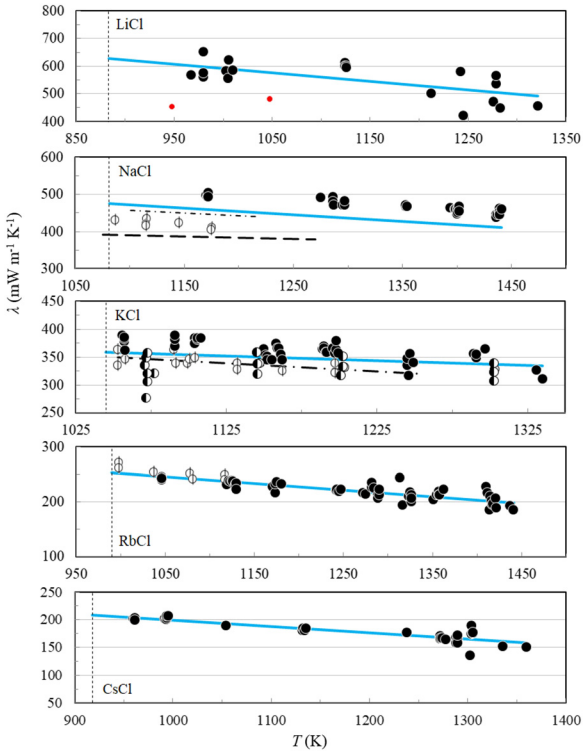

FIG. 6. Primary data and previous reference values for the thermal conductivity of LiCl, NaCl, KCl, RbCl, and CsCl as a function of the temperature. Nagasaka *et al.*[4] (●), Golyshev and Gonik[3] (—·—), Harada *et al.*[6] (ϕ), Nagasaka and Nagashima[17] (◐), Veneraki *et al.*[8] (— —). Equation (1) (blue line) and previous reference values of Janz *et al.*[11] (red filled circle); melting temperature (- -).

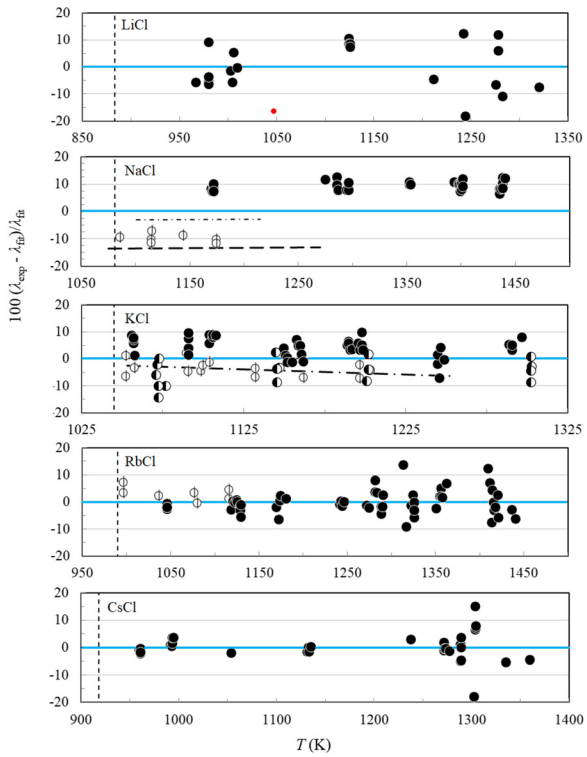

FIG. 7. Percentage deviations of the primary data for the thermal conductivity of LiCl, NaCl, KCl, RbCl, and CsCl from the values produced by Eq. (1), as a function of the temperature. Nagasaka *et al.*[4] (●), Golyshev and Gonik[3] (—·—), Harada *et al.*[6] (ϕ), Nagasaka and Nagashima[17] (◐), Veneraki *et al.*[8] (— —), and reference values of Janz *et al.*[11] (red filled circle); melting temperature (- -).

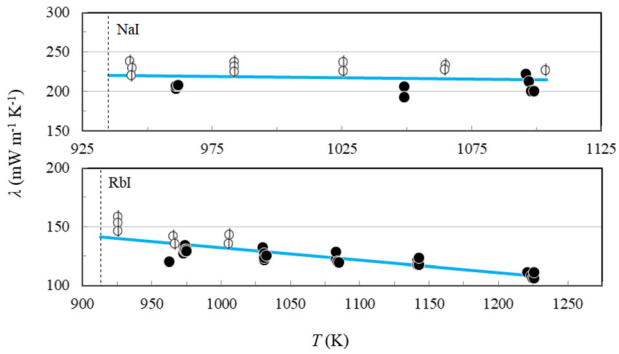

FIG. 8. Primary data for the thermal conductivity of NaI and RbI as a function of the temperature. Harada *et al.*[6] (ϕ), Nakazawa *et al.*[19] (●), and Eq. (1) (blue line); melting temperature (- -).

in Fig. 8. As in the case of the molten bromide salts discussed in Sec. 4.2 and following the discussion of Sec. 2, only two primary data sets (Harada *et al.*[6] and Nakazawa *et al.*[19]) are considered for each iodide salt. No previous reference correlation exists, to our knowledge. The data were correlated according to Eq. (1), and the coefficients together with the uncertainty of each correlation are shown in Table 5. Figure 9 shows the percentage deviations of the primary data sets from the values calculated by Eq. (1) and the corresponding coefficients of Table 5.

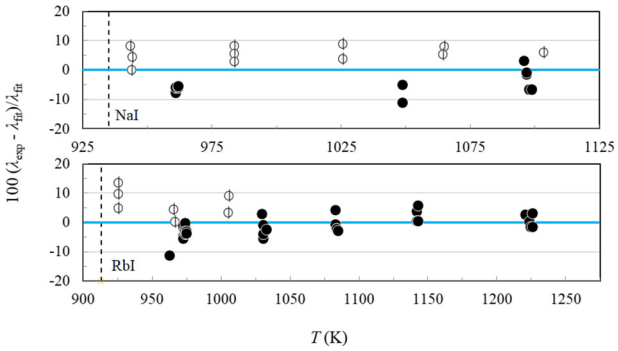

FIG. 9. Percentage deviations of the primary data for the thermal conductivity of NaI and RbI from the values produced by Eq. (1), as a function of the temperature. Harada *et al.*[6] (Φ) and Nakazawa *et al.*[19] (●); melting temperature (- -).

4.5. Proposed values

In Tables 6–9, recommended values are given for the 13 molten salts studied in this work. These values are calculated employing Eq. (1) with the coefficients and parameters shown in Table 5.

TABLE 6. Recommended values for the thermal conductivity of molten $LiNO_3$, $NaNO_3$, and KNO_3 as a function of temperature at 0.1 MPa. Estimated uncertainties at the 95% confidence level are $LiNO_3$ (7%), $NaNO_3$ (7%), and KNO_3 (15%)

	λ (mW m^{-1} K^{-1})		
T (K)	**$LiNO_3$**	**$NaNO_3$**	**KNO_3**
530	572		
550	569		
575	566		
600	562	517	
625		513	424
650		510	413
675		507	403
700		503	392
725			382

TABLE 7. Recommended values for the thermal conductivity of molten NaBr, KBr, and RbBr as a function of temperature at 0.1 MPa. Estimated uncertainties at the 95% confidence level are NaBr (15%), KBr (15%), and RbBr (15%)

	λ (mW m^{-1} K^{-1})		
T (K)	**NaBr**	**KBr**	**RbBr**
975			203
1000			200
1025	318	226	197
1050	315	224	195
1075	313	221	192
1100	311	219	189
1125	309	217	186
1150	307	215	184
1175	305	212	181
1200	303	210	178
1225	301	208	175
1250	298	206	173
1275	296		170
1300			167
1325			164

TABLE 8. Recommended values for the thermal conductivity of molten LiCl, NaCl, KCl, RbCl, and CsCl as a function of temperature at 0.1 MPa. Estimated uncertainties at the 95% confidence level are LiCl (17%), NaCl (20%), KCl (17%), RbCl (17%), and CsCl (10%)

	λ (mW m^{-1} K^{-1})				
T (K)	**LiCl**	**NaCl**	**KCl**	**RbCl**	**CsCl**
900	623				
950	607				205
1000	592			253	199
1050	576		359	246	194
1100	561	472	355	240	188
1150	545	463	350	234	182
1200	530	454	346	228	176
1250	514	445	342	222	171
1300	499	436	338	216	165
1350	483	427	333	210	159
1400		418		203	153
1450		409		197	

TABLE 9. Recommended values for the thermal conductivity of molten NaI and RbI as a function of temperature at 0.1 MPa. Estimated uncertainties at the 95% confidence level are NaI (17%) and RbI (20%)

	λ (mW m^{-1} K^{-1})	
T (K)	**NaI**	**RbI**
925		140
950	220	137
975	219	134
1000	218	132
1025	217	129
1050	216	126
1075	215	124
1100	214	121
1125		118
1150		116
1175		113
1200		110
1225		108

5. Conclusions

The available experimental data for the thermal conductivity of 13 inorganic molten salts have been critically examined and new thermal-conductivity reference correlation were proposed. Standard reference correlations were proposed for the following molten salts (with estimated uncertainties at the 95% confidence level given in parentheses): $LiNO_3$ (7%), $NaNO_3$ (7%), KNO_3 (15%), NaBr (15%), KBr (15%), RbBr (15%), LiCl (17%), NaCl (20%), KCl (17%), RbCl (17%), CsCl (10%), NaI (17%), and RbI (20%).

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