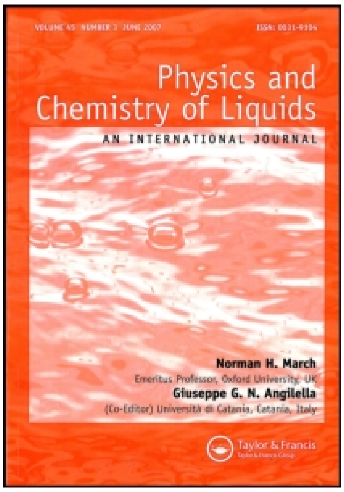


Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Bounds of Complex Formation for Alkali-Earth Cation in Molten Alkali Chlorides

Kazuo Sakai[a]; Tetsurō Nakamura[a]; Norimasa Umesaki[b]; Nobuya Iwamoto[b]
[a] Research Laboratory of Engineering Materials, Tokyo Institute of Technology, Yokohama-shi, Japan [b] Welding Research Institute, Ōsaka University, Suita-shi, Japan

To cite this Article Sakai, Kazuo , Nakamura, Tetsurō , Umesaki, Norimasa and Iwamoto, Nobuya(1984) 'Bounds of Complex Formation for Alkali-Earth Cation in Molten Alkali Chlorides', Physics and Chemistry of Liquids, 14: 1, 67 — 78

To link to this Article: DOI: 10.1080/00319108408080797

URL: http://dx.doi.org/10.1080/00319108408080797

Phys. Chem. Liq., 1984, Vol. 14, pp. 67–78
0031-9104/84/1401-0067$18.50/0

Bounds of Complex Formation for Alkali-Earth Cation in Molten Alkali Chlorides

KAZUO SAKAI and TETSURŌ NAKAMURA
Research Laboratory of Engineering Materials, Tokyo Institute of Technology, Nagatsuta 4259, Yokohama-shi 227, Japan.

and

NORIMASA UMESAKI and NOBUYA IWAMOTO
Welding Research Institute, Ōsaka University, Suita-shi 565, Japan.

(*Received December 5, 1983*)

The tendency of alkali-earth cation $M^{2+}(M = \text{Be, Mg, Ca, Sr, Ba})$ to form a complex ion in molten alkali chlorides ACl ($A = \text{Li, Na, K, Rb, Cs}$) has been interpreted in terms of attractive Coulomb interactions between the cation and anion; $\Delta\Phi = \Phi(\text{MCl}) - \Phi(\text{ACl})$. The experimental results by means of the Laser Raman spectroscopy indicated the presence of some complex ion in the molten ACl-MCl_2 systems only when $\Delta\Phi \gtrsim 0.38$. Coexistence of an octahedral and a tetrahedral complex ions, $[CaCl_6]^{4-}$ and $[CaCl_4]^{2-}$, has been suggested via deconvolution of Raman band in the molten $2KCl \cdot CaCl_2$ composition.

INTRODUCTION

Raman spectral studies of the molten ACl-MCl_2 systems, where A is an alkali metal and M is an alkali-earth metal, have been scarcely presented except for the cases $M^{2+} = Be^{2+}$ and Mg^{2+}, because of their weak intensities with the strong stray lights on account of their high melting points. Among various interactions in a molten ionic salt, ACl or MCl_2, there is only one kind of attractive Coulomb interaction between the cation and anion, $\Phi(\text{ACl})$ or $\Phi(\text{MCl})$, which is essential to the cohesion of the molten salt. In the molten ACl-MCl_2 system, however, the two kinds of attractive Coulomb interactions coexist and their difference $\Delta\Phi = \Phi(\text{MCl}) - \Phi(\text{ACl})$ produces a heterogeneity in cohesion of the moten system, causing to form a complex ion about M^{2+} ion. Making use of the concept of "ionic radii," the relative tendency of M^{2+} cation to form a complex ion in the molten ACl-MCl_2 system is defined here by

$$\Delta\Phi = \Phi(\mathrm{MCl}) - \Phi(\mathrm{ACl}) = \frac{|Z_M Z_{Cl}|}{r_M + r_{Cl}} - \frac{|Z_A Z_{Cl}|}{r_A + r_{Cl}} \qquad (1)$$

where the octahedral ionic radii proposed by Shannon[1] are employed for the values of r_A, r_M and r_{Cl}, and $Z_A = 1$, $Z_M = 2$ and $Z_{Cl} = -1$ are ionic valences. Table I indicates the values of Φ(ACl), Φ(MCl) and $\Delta\Phi$ for every ACl-MCl_2 system.

The existence of complex ions has been reported only for the molten ACl-MCl_2 systems with $M^{2+} = Be^{2+}$[2] and Mg^{2+}[3-9], which have values of $\Delta\Phi$ greater than 0.4 in Table I. Looking into Table I, one can expect a complex formation also in the cases of $M^{2+} = Ca^{2+}$ owing to their values $\Delta\Phi \geq 0.4$. Thus, we have examined a complex formation for cases $M^{2+} = Ca^{2+}, Sr^{2+}, Ba^{2+}$ by means of the Laser Raman spectroscopy.

EXPERIMENT

The reagents of $CaCl_2$, $SrCl_2$, $BaCl_2$ and alkali chlorides were purified by the following method. After heating in a vacuum for several days, the chlorides (purity 99.9%) of $MCl_2(M^{2+} = Ca^{2+}, Sr^{2+}, Ba^{2+})$ and $ACl(A^+ = Li^+, Na^+, K^+, Rb^+, Cs^+)$ were mixed in the ratio 1:2 and transferred into a quartz-tube for purification. The tube containing chloride mixture was heated in an electric furnace up to the temperature by 100°C lower than the melting point in an Ar atmosphere, followed by removing Ar gas with HCl gas and raised up the temperature by 50°C higher than the melting point. The HCl gas was continued to bubble through the molten sample until it became a colorless, transparent liquid. Then, the sample was transferred into the Raman cell of 10ϕ diameter whose bottom was polished to be a flatness of optical grade.

Raman spectra were recorded by JEOL spectrophotometer after sample excitation with 514.5nm (ca. 800 mW at the sample) of an Ar^+ ion Laser (Spectra Physics Co.).

RESULTS AND DISCUSSION

ACl-$CaCl_2$ Systems

Figure 1 shows a Raman spectrum of solid $CaCl_2$ at room temperature. Since $CaCl_2$ has a Rutile structure, Ca^{2+} cation is centered at a slightly distorted octahedron composed of six Cl^- anions. Therefore, the Raman peaks in

Figure 1 have been attributed to those of local vibrational modes A_{1g}(266 cm^{-1}), Eg(215 cm^{-1}) and T_{2g}(157 cm^{-1}) from [$CaCl_6$]-octahedron.

Figure 2 indicates the Raman spectra for both polycrystalline and molten $2ACl \cdot CaCl_2$. According to Seifert,[10] solid $2CsCl \cdot CaCl_2$ crystallizes in a K_2NiF_4-structure with a distorted [$CaCl_6$]-octahedron, belonging to the space group $I_{4/mmm}$. An excellent discussion on the structure of solid $2KCl \cdot MgCl_2$ by Brooker,[7] resulted in the same space group $I_{4/mmm}$, although he could not observe A_{1g} mode in his Raman spectra. As shown in Figure 2, we have observed a weak line at 263 cm^{-1} in the Raman spectrum of polycrystalline $2CsCl \cdot CaCl_2$, which is attributable to the mode of A_{1g} because of a correspondence of the mode in solid $CaCl_2$ at 266 cm^{-1} in Figure 1. Judging from the assignment for solid $2KCl \cdot MgCl_2$[7], the two strong peaks at 190 cm^{-1} and 68 cm^{-1} in Figure 2e may be assigned to Eg modes, and a weak one at 155 cm^{-1} to T_{2g} mode from local [$CaCl_6$]-octahedron.

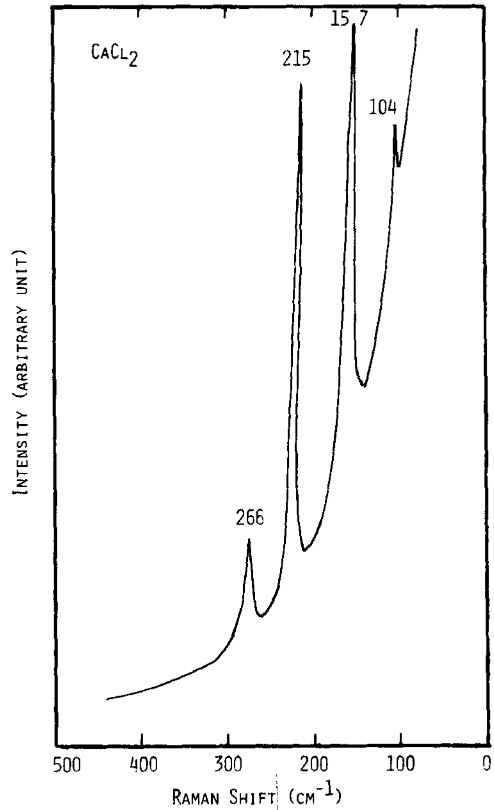


FIGURE 1 Raman spectrum of polycrystalline $CaCl_2$. Raman frequency for each peak is denoted in the figure.

TABLE I

Attractive Coulomb interactions for A^+-Cl^- pair Φ(ACl), M^{2+}-Cl^- pair Φ(MCl) and their difference ΔΦ in (electronic charge)^2. A^{-1}

	ΦACl	0.389	0.353	0.313	0.300	0.287
ΦMCl	ΔΦ	Li^+	Na^+	K^+	Rb^+	Cs^+
0.885	Be^+	0.496	0.532	0.572	0.585	0.598
0.791	Mg^+	0.402	0.438	0.478	0.490	0.504
0.712	Ca^+	0.323	0.359	0.399	0.412	0.425
0.669	Sr^+	0.280	0.316	0.356	0.369	0.382
0.633	Ba^+	0.244	0.280	0.320	0.333	0.346

In Table II are listed the Raman frequency data for solid $2ACl \cdot CaCl_2$ and the force constants for $[CaCl_6]$-octahedron based on the assignment mentioned above. The remaining peaks in Figures 1 and 2, lacking of the description in Table I, may be attributable to those from lattice vibrations.

As is seen in Figures 2-a and 2-b, no remarkable Raman peaks or hills have been detected but only a slight bulge around 200 cm^{-1} on the Raylei slope for melt composition $2LiCl \cdot CaCl_2$ and $2NaCl \cdot CaCl_2$. The evidence of very weak totally symmetric stretching vibrations in those molten systems implies that very few of Ca^{2+} cation form complex ions with the surrounding Cl^{-1} anions. In the case of melt composition $2KCl \cdot CaCl_2$ in Figure 2c, on the other hand, an appreciable envelope of Raman peaks exists, although no useful informations were obtained from depolarization experiments.

This envelope of Raman peaks for $2KCl \cdot CaCl_2$ melt could be divided into four components, as shown in Figure 3, with a nonlinear least-squares method using the Voigt function, i.e., a convolution of Lorentzian and Gaussian functions.†

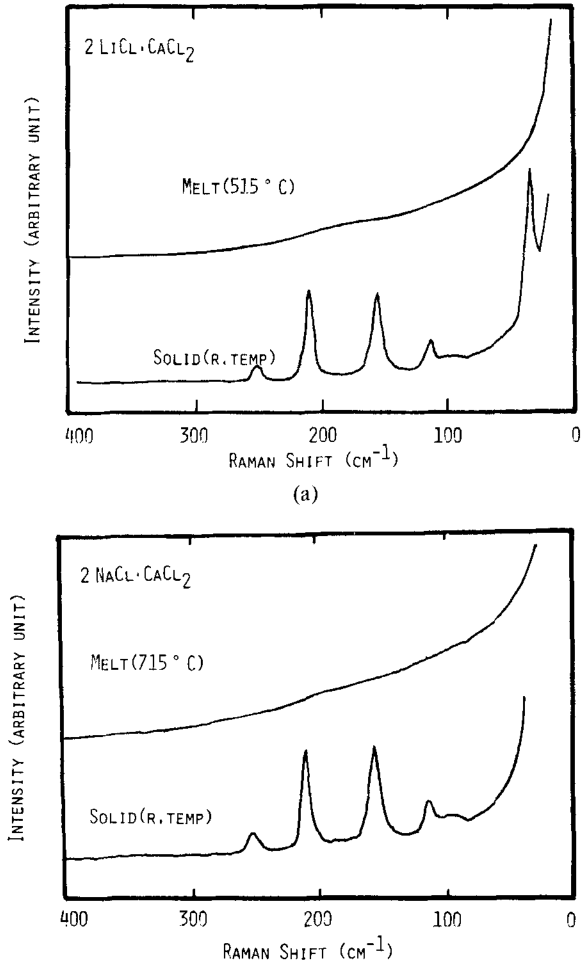
Raman frequencies of the divided components for molten $2KCl \cdot CaCl_2$ in Figure 3 are 257 cm^{-1}, 224 cm^{-1}, 199 cm^{-1} and 146 cm^{-1}. The respective components 257 cm^{-1}, 199 cm^{-1} and 146 cm^{-1} well coincide with the Raman peaks 255 cm^{-1}, 198 cm^{-1} and 130 cm^{-1} from $[CaCl_6]$-octahedron of the solid $2KCl \cdot CaCl_2$ in Table II. If one remembers the anomalies at the molar fraction $X = 1/3(2KCl \cdot CaCl_2)$ in the enthalpy interaction parameter $\Delta H^M/X(1 - X)$[11] and in the partial molar entropies of mixing $\Delta\bar{S}_{CaCl_2}$ in the

---

† The details of the method for peak division will be presented in the separate paper.

molten KCl-$CaCl_2$ system, the remained strong component 224 cm^{-1} in Figure 3 can be ascribed to the Raman peak from a tetrahedral complex ion $[CaCl_4]^{2-}$ in the molten 2KCl · $CaCl_2$.

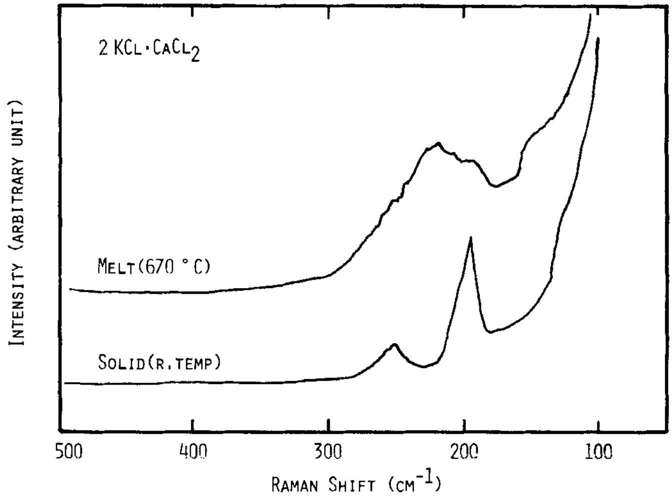
In the case of molten 2RbCl · $CaCl_2$, broad and weak Raman spectra are detectable in Fig. 2d at the region 160 ~ 280 cm^{-1} and at 320 cm^{-1} and 360 cm^{-1}. The assignment of these spectra was not made yet. In the case of 2CsCl · $CaCl_2$, however, no appreciable Raman lines were observed owing to a high temperature. We guess that any peaks will be observable under a better condition.



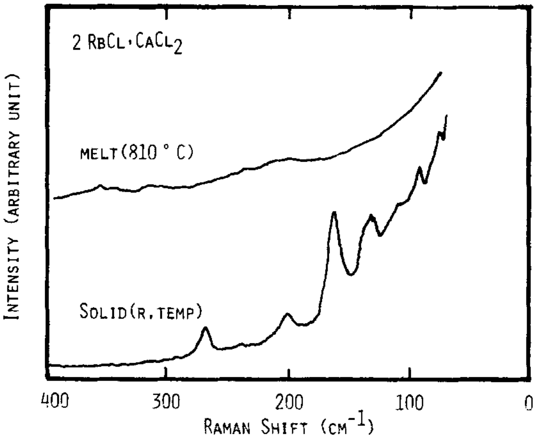
(a)

(b)

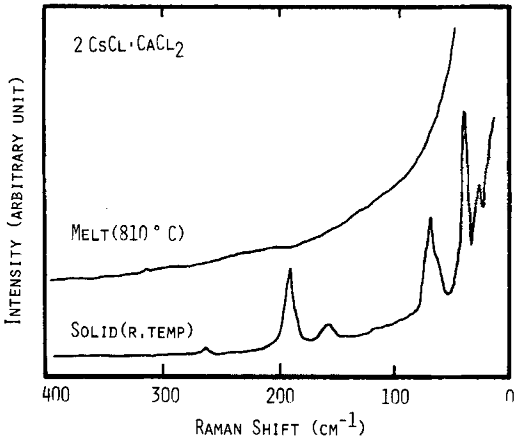
FIGURE 2a,b (*Caption see over*)


2 KCl·CaCl2
Melt(670 °C)
Solid(r.temp)
Intensity (arbitrary unit)
500
400
300
200
100
Raman Shift (cm-1)

(c)


2 RbCl·CaCl2
melt(810 °C)
Solid(r.temp)
Intensity (arbitrary unit)
400
300
200
100
0
Raman Shift (cm-1)

(d)



(e)

FIGURE 2 Raman spectra for polycrystalline and molten 2ACl · $CaCl_2$ composition. The experimental temperatures are indicated in each figure. a) A = Li, b) A = Na, c) A = K, d) A = Rb, e) A = Cs.

TABLE II

Observed Raman spectral lines in solid $CaCl_2$ and 2ACl·$CaCl_2$ and their force constants for $[CaCl_6]$-octahedra calculated via modified Urey-Bradley method

	Normal frequencies/cm^{-1}			Force constants/mdyn · A^{-1}		
	$\nu_{A_{1g}}$	ν_{E_g}	$\nu_{T_{2g}}$	K	H	F^*
$CaCl_2$	266	215	157	0.857	0.0434	0.155
2ACl·$CaCl_2$						
A = Li	252	212	157	0.845	0.0624	0.120
Na	253	210	158	0.832	0.0608	0.126
K	255	198	130	0.701	0.0014	0.163
Rb	270	200	163	0.690	0.0243	0.208
Cs	263	190	155	0.603	0.0098	0.210

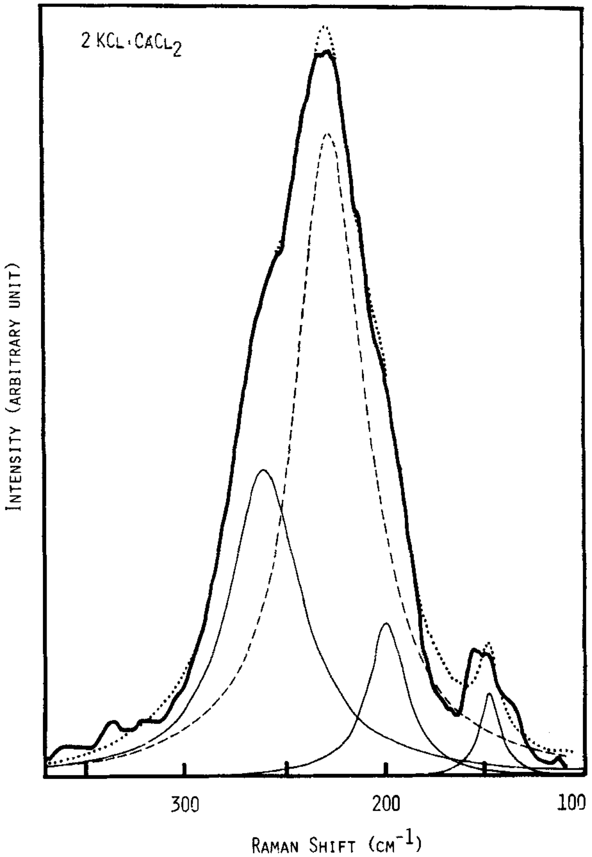


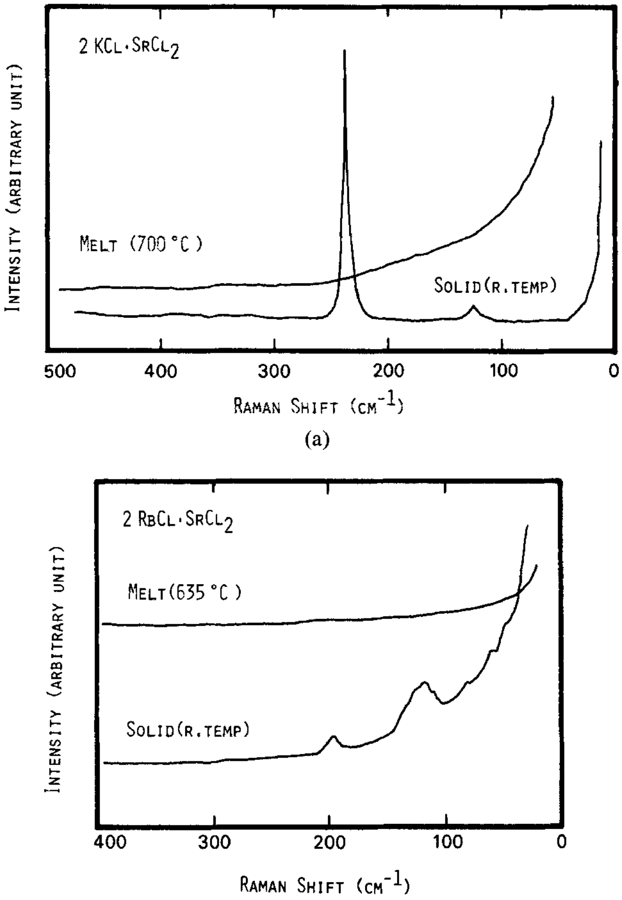
FIGURE 3 The observed Raman spectrum of molten $2KCl \cdot CaCl_2$ divided into four components: —— observed, · · · · · composed, —— the three components from $[CaCl_6]$-octahedron, $\nu = 146\ cm^{-1}$, $\nu = 199\ cm^{-1}$ and $\nu = 257\ cm^{-1}$, ------ the fourth component $\nu = 224\ cm^{-1}$ probably from $[CaCl_4]$-tetrahedron.

The results and discussions mentioned above conclude that Ca^{2+} cation forms a complex ion in the molten KCl($\Delta\Phi = 0.399$ in Table I), RbCl($\Delta\Phi = 0.412$) and CsCl($\Delta\Phi = 0.425$), and does not in the molten LiCl($\Delta\Phi = 0.323$) and NaCl($\Delta\Phi = 0.359$).

ACl-$SrCl_2$ systems

Figure 4 shows the Raman spectra of $2ACl \cdot SrCl_2(A^+ = K^+, Rb^+, Cs^+)$ and $4CsCl \cdot SrCl_2$ compositions in the solid state and the molten state. In the molten compositions of $2KCl \cdot SrCl_2$ and $2RbCl \cdot SrCl_2$, no distinct Raman peaks could be observed, while in the molten composition $2CsCl \cdot SrCl_2$, the weak peaks are detected at the frequency regions 240 ~ 280 cm^{-1} and 170 ~ 250 cm^{-1}. Furthermore, a distinct peak or an envelope of peaks was observed at region 170 ~ 250 cm^{-1} in the case of molten composition $4CsCl \cdot SrCl_2$. This spectrum might correspond to a peak at 200 cm^{-1} in the solid state, but no clear explanation could be made because of the violent stray lights covered strongly the spectrum in the frequency range higher than the 250 cm^{-1}.

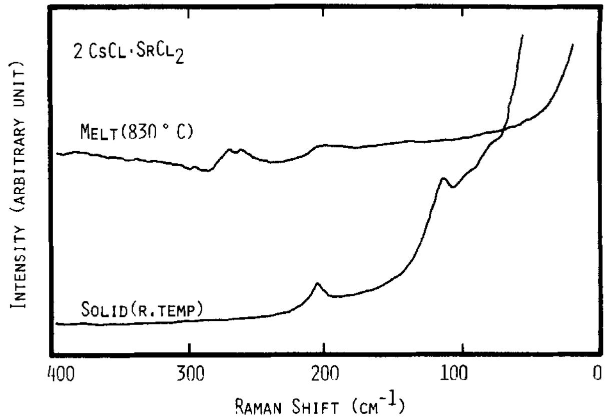
The results conclude that Sr^{2+} cation forms a complex ion only in the molten $CsCl(\Delta\Phi = 0.382$ in Table I) but does not in the molten $KCl(\Delta\Phi = 0.356)$ and $RbCl(\Delta\Phi = 0.369)$.



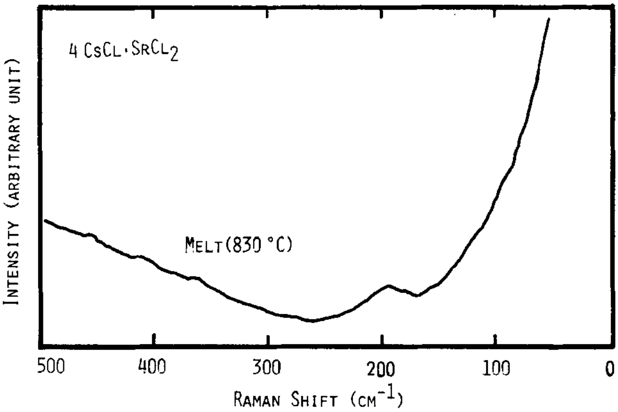
(a)

(b)

FIGURE 4a,b (*Caption see over*)



(c)



(d)

FIGURE 4 Raman spectra for polycrystalline and molten a) $2KCl \cdot SrCl_2$, b) $2RbCl \cdot SrCl_2$, c) $2CsCl \cdot SrCl_2$ and d) $4CsCl \cdot SrCl_2$ compositions. The experimental temperatures are indicated in each figure.

KCl-$BaCl_2$ system

Figure 5 shows the Raman spectra of the composition $2KCl \cdot BaCl_2$ in the solid state and the molten state. The result indicates that Ba^{2+} cation does not form any complex ion in the molten KCl. Moreover, Ba^{2+} cation may not form a complex ion in all the other molten alkali chlorides according to the values $\Delta\Phi > 0.38$ in Table I.

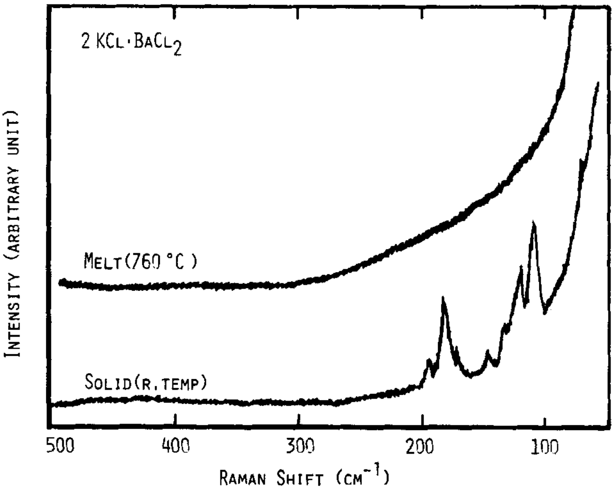


FIGURE 5 Raman spectra for polycrystalline and molten 2KCl · $BaCl_2$ composition. The experimental temperatures are indicated in the figure.

CONCLUSION

The experimental results of Raman spectral studies and the inference from attractive Coulomb interactions in Table I conclude that the cation M^{2+} forms a complex ion in the molten ACl-MCl_2 systems ($A^+ = Li^+, Na^+, K^+, Rb^+, Cs^+$; $M^{2+} = Ca^{2+}, Sr^{2+}, Ba^{2+}$) only when $\Delta\Phi > 0.38$.

Acknowledgements

The two authors wish to express their hearty thanks to Professor K. Kawamura, Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, to Professor S. Maeda and Dr. S. Kobinata, Research Laboratory of Resources Utilization, Tokyo Institute of Technology, and to Professor M. Uemura, Tokyo Institute of Polytechnics, for their kind instructions, permission to use their Laser Raman spectrophotometer and useful discussions.

Thanks are also due to Dr. N. Itoh, Research Laboratory of Engineering Materials, Tokyo Institute of Technology, for her kind constructions and corrections of this paper.

References

1. R. D. Shannon, *Acta. Cryst.*, **A32**, 751 (1976).
2. V. D. Prisyaginii, S. P. Baranov, and G. P. Sunegin, *Zh. Neorg. Khim.*, **23**, 1678 (1978).
3. K. Balasubrahmanyam, *J. Chem. Phys.*, **44**, 3270 (1966).
4. V. A. Maroni, E. J. Hathaway, and E. J. Cairns, *J. Phys. Chem.*, **75**, 155 (1971).
5. V. A. Maroni, *J. Chem. Phys.*, **55**, 4789 (1971).
6. R. J. Capwell, *Chem. Phys. Lett.*, **12**, 443 (1972).

7. M. H. Brooker, *J. Chem. Phys.*, **63**, 3054 (1975).
8. C.-H. Huang and M. H. Brooker, *Chem. Phys. Lett.*, **43**, 180 (1976).
9. M. H. Brooker, and C.-H. Huang, *Can. J. Chem.*, **58**, 168 (1980).
10. H. J. Seifert and U. Langenbach, *Z. Anorg. Allgem. Chem.*, **368**, 36 (1969).
11. T. Østvold, *J. Phys. Chem.*, **76**, 1616 (1972).
12. T. Østvold, *Temp. Sci.*, **4**, 51 (1972).