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Raman Studies of Complex Ions in $ThCl_4$–KCl Melt Using Raman Bands Shifts

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Raman spectra of solid and molten $ThCl_4$–KCl system were observed and the structure change of $ThCl_4$ on melting from the octa-coordinate body-centered tetragonal type, D_{4h}, to the tetra-coordinate tetrahedron type, T_d, was studied. The decrease in frequency of the symmetric stretching vibration ν_1 with decrasing $ThCl_4$ concentration for molten $ThCl_4$–KCl is interpreted as due to the presence of $ThCl_4$, $ThCl_5^-$, and $ThCl_7^{3-}$ complexes in the molten $ThCl_4$–KCl mixture. Such a compositional dependence for ν_1 appears to support the idea that, for a decrease in the $ThCl_4$ concentration in molten $ThCl_4$–KCl mixtures, the bond strength between the thorium and chloride ions decreases and the number of chloride ions around the thorium ion increases from 4 to 7.

Various physical properties, such as electromotive force,[1] density,[2] equivalent conductivity,[2] and viscosity[3] for the $ThCl_4$– KCl system, have been measured as fundamentally important data for the electrolytic preparation of thorium metal. In the variation of these physical isothermal properties with $ThCl_4$ concentration, deviations from the additivity line have been attributed to the existence of a complex ion, since the concentration giving the maximum deviation corresponds to that of a congruently melting compound.

In this paper, the formation and structure of complex ions in the $ThCl_4$–KCl system are discussed on the basis of the variation of the Raman bands of solid and molten $ThCl_4$–KCl systems with concentration.

Experimental

Samples. *Thorium Tetrachloride*: As described in a previous report,[4] thorium(IV) chloride was refined by vacuum fractional distillation.

Potassium Chloride: Potassium chloride of special reagent grade was melted, bubbled with dry hydrogen chloride, and the retained HCl was purged by purified argon. The melt was evacuated using a rotary pump for one hour to remove the argon.

Samples: Weighed amounts of thorium and potassium chlorides were melted and mixed in a quartz cell in an HCl atmosphere, and then the mixture was poured into the measuring cell *in vacuo*. The thorium concentration of these samples was corrected by chemical analysis after measuring the spectra.

Apparatus. Raman spectra were recorded with a Spex Model 1401 Ramalog 4 spectrometer. A Coherent Radiation Model 52 488-nm argon-ion laser was used. The furnace temperature for the molten salts was controlled to within ±0.5 °C.

Results and Discussion

Raman Spectra of Pure Thorium Chloride. The Raman spectra of rapidly quenched solid and molten thorium chloride were recorded from 50 to 2000 cm^{-1} at room temperature and at 800 °C, respectively. The Raman bands of solid thorium chloride were found at 296, 182, and 259 cm^{-1} and those of molten thorium chloride at 334, 132, and 270 cm^{-1}, as listed in Table 1.

Table 1. Raman bands for pure $ThCl_4$

Band (cm^{-1}) for $ThCl_4$		Assignment
solid	melt	
296	334	$\nu_1(A_1)$
182	132	$\nu_2(E)$
—	—	$\nu_3(F_2)$
259	270	$\nu_4(F_2)$

The crystal structure of thorium(IV) chloride has been reported to be a body-centered tetragonal structure (D_{4h}) as shown in Fig. 1.[5] The number of chloride ion around the thorium(IV) ion is eight. The four Cl^- ions are close to the Th^{4+} ion (2.718 Å) and form a square planar configuration. The remaining four Cl^- ions are far from the Th^{4+} ion (2.903 Å) and form a distorted tetrahedron. Each Th^{4+} ion is dodecahedrally coordinated in a crystal lattice. In the quenched state, pure thorium chloride does not have a stable crystalline form, but is a tetrahedron with a slightly deformed body-centered tetragonal framework resulting from the strong mutual interaction between the four Cl^- ions and the near Th^{4+} ion.[6] Thus, the structure of pure $ThCl_4$ may change from an octa-coordinate body-centered tetragonal structure, D_{4h}, to a tetra-coordinate tetrahedron structure, T_d, upon melting. The Raman band at 334 cm^{-1} for pure molten $ThCl_4$ can be assigned to a symmetric stretching vibration of T_d symmetry, and the other bands at 132 and 270 cm^{-1} to bending vibrations of

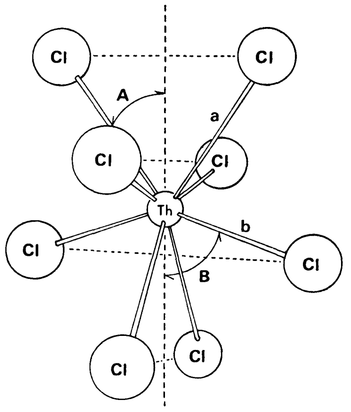

Fig. 1. Coordination about the Th atom in the $ThCl_4$ (D_{4h}) structure.
A: 33.1°, B: 78.0°, a: 2.903 Å, and b: 2.718 Å.

T_d symmetry.[7] The assignments of bands for pure solid $ThCl_4$ listed in Table 1 are in analogy to the assignments for molten $ThCl_4$.

Table 1 shows the band shifts to higher frequencies upon melting. These shifts can be explained if four Cl^- ions far from Th^{4+} ion become free, and the four Cl^- ions near Th^{4+} ion are strongly attracted to the Th^{4+} ion by the strong polarization force. In other words, the strong interaction between the Th^{4+} and Cl^- ions resulting from a decrease in the interionic distance can explain the shifts of the Raman bands toward higher frequencies upon melting.

The Raman bands for ThO_2 which have been reported at 460 cm^{-1} [8] were not observed. No evidence for the existence of $ThOCl_2$ in pure solid $ThCl_4$ was obtained. These facts are also supported by failure to detect any ThO_2 or $ThOCl_2$ upon chemical analysis.

Raman Spectra of the Solid $ThCl_4$–KCl System. Raman spectra of the solid $ThCl_4$–KCl system were obtained over the range from 50—2000 cm^{-1} at room temperature (Fig. 2 and Table 2).

The frequencies for the solid $ThCl_4$–KCl system with 1.0—0.10 molar fractions of thorium chloride remain almost constant. The Raman bands at 250 cm^{-1} and near 280 cm^{-1}, which are obtained for $ThCl_4$ molar fractions of 0.34—0.62, are also observed in the solid form containing $ThCl_4$ molar fractions above 0.62 and below 0.34, respectively. Moreover, the discontinuous variation of Raman bands near 300 cm^{-1} with $ThCl_4$ concentration is illustrated in the phase diagram for $ThCl_4$ and KCl, as shown in Fig. 3. This spectral variation with concentration appears to support the presence of a $ThCl_4$ compound with a molar fraction from 1.0—0.62, of a congruently melting compound $KThCl_5$ with a molar fraction of 0.62—0.34, and K_3ThCl_7 with a molar fraction of 0.34—0.10 of $ThCl_4$. Aside from the existence of K^+ ions, it may be assumed by analogy with $KThF_5$[9] and K_3UF_7,[10] that the $ThCl_5^-$ and $ThCl_7^{3-}$ species have trigonal bipyramidal and pentagonal bipyramidal structures, respectively. The symmetric stretching vibration, ν_1, are easily assigned for the $ThCl_4$, $ThCl_5^-$, and $ThCl_7^{3-}$ species, but the assignments of other modes of vibration are quite difficult due to the structural complexities of the above species. Table 2 shows that the frequency of the ν_1 vibration decreases with the $ThCl_4$ concentration from 1.0 to 0.1 molar fraction, suggesting the presence of two congruently melting compounds.

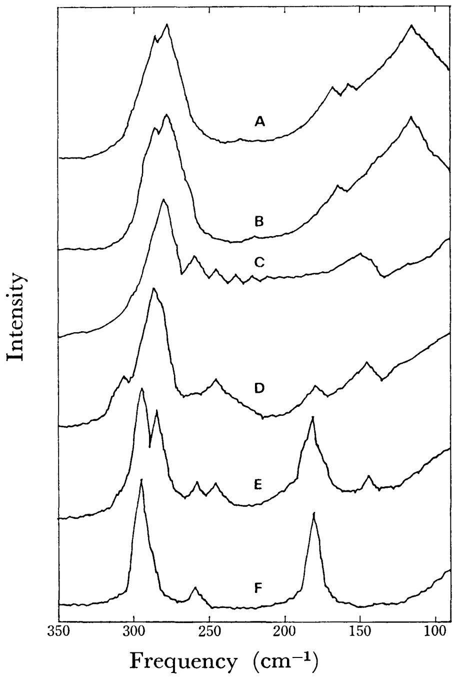

Fig. 2. Raman spectra of the solid $ThCl_4$–KCl system. $ThCl_4$ concentrations (mole fraction): A: 0.10, B: 0.25, C: 0.34, D: 0.50, E: 0.62, and F: 1.00.

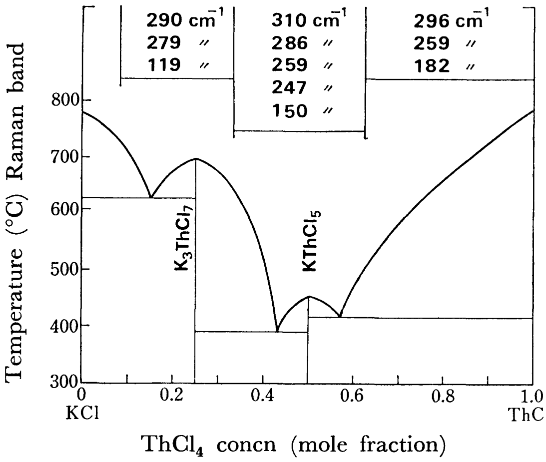

Fig. 3. The relation between Raman bands and the phase diagram for the $ThCl_4$–KCl system.

Raman Spectra of the Molten $ThCl_4$–KCl System. Raman spectra of the molten $ThCl_4$–KCl system were observed over the range 50—2000 cm^{-1} at 800 °C. The spectra for melts containing 1.00—0.25 molar fractions of $ThCl_4$ are shown in Fig. 4 and Table 3. The second column in Table 3 lists also the polarization of each band. While the bands for a 0.5 molar

TABLE 2. RAMAN BANDS FOR THE SOLID $ThCl_4$-KCl SYSTEM

$ThCl_4$ concn (mol frac.)	Raman band in cm^{-1} (± 1.0 cm^{-1})							
1.0	—	296(ν_1)	—	259	—	182	—	—
0.6	310	296(ν_1)	285	259	247	182	149	—
0.50	310	—	286(ν_1)	259	247	—	150	—
0.34	310	—	280(ν_1)	259	247	—	150	—
0.25	—	290	279(ν_1)	—	—	—	—	119
0.10	—	289	279(ν_1)	—	—	—	—	119

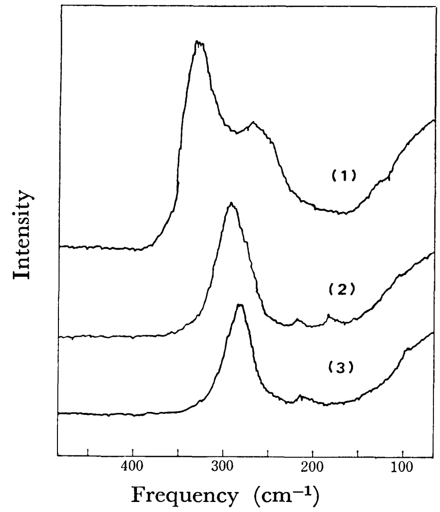

Fig. 4. Raman spectra of molten $ThCl_4$-KCl system at 800 °C with $ThCl_4$ concn compositions (mole fraction): (1): 1.0, (2): 0.50, and (3); 0.25.

Table 3. Raman bands for the molten $ThCl_4$-KCl

$ThCl_4$ concn (mol frac.)	Raman band (cm^{-1})	Polarization	Assignment
1.00	334	polar	$\nu_1(A_1)$
($ThCl_4$)	132	depol	$\nu_2(E)$
	—	depol	$\nu_3(F_2)$
	270	depol	$\nu_4(F_2)$
0.50	293	polar	$\nu_1(A')$
($ThCl_5^-$)	—	polar	$\nu_2(A_1')$
	213	depol	$\nu_5(E')$
	187	depol	$\nu_7(E')$
	113	depol	$\nu_8(E'')$
0.25	283	polar	$\nu_1(A')$
($ThCl_7^{3-}$)	—	polar	$\nu_2(A')$
	98	depol	$\nu_8(E_2')$
	—	depol	$\nu_9(E_2')$
	219	depol	$\nu_{10}(E_1'')$

fraction of $ThCl_4$ are observed at 293, 219, 187, and 113 cm^{-1}, the bands for a 0.25 molar fraction are observed at 285, 219, and 98 cm^{-1}. As shown in Fig. 3, these compositions of 0.5 and 0.25 molar fractions correspond to those of congruently melting compounds. It should be noted that the wave numbers of Raman bands for a certain concentration range (0.1—0.3 molar frac.) near each congruently melting compound remain almost constant. The above fact suggests the presence of $ThCl_5^-$ and $ThCl_7^{3-}$ complex ions for the melts containing 0.5 and 0.25 molar fractions of $ThCl_4$, respectively. Since the complex ions $ThCl_5^-$ and $ThCl_7^{3-}$ are assumed to have trigonal bipyramidal and pentagonal bipyramidal structures, respectively, the assignments based on these structures are listed in Table 3. From the compositional dependence of the stretching vibration, ν_1, shown in Fig. 5, it is indicated that ν_1 decreases with $ThCl_4$ concentration. Such a compositional dependence of ν_1 appears to support the idea that for decreasing $ThCl_4$ concentration the bond strength between the thorium(IV) ion and chloride ion decreases and the coordination state for thorium(IV) varies from four, to five and seven coordinations. In these binary mixtures with a common anion, the variations of bond strength and thorium coordination number can be ascribed to a change in the polarization force.

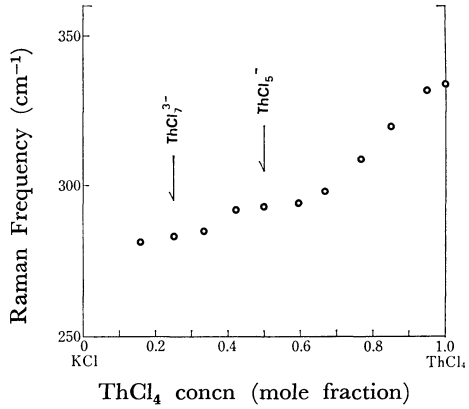

Fig. 5. Frequency shifts of ν_1 band with $ThCl_4$ concentration change in a molten $ThCl_4$–KCl system.

References

1) S. Yoshida and T. Kuroda, *Denki Kagaku*, **41**, 217 (1973).

2) S. Yoshida, T. Ayano, and T. Kuroda, *Denki Kagaku*, **41**, 427 (1973).

3) S. Yoshida, S. Kaji, and K. Kawamura, *Denki Kagaku*, **43**, 195 (1975).

4) S. Yoshida, R. Oyamada, and T. Kuroda, *Denki Kagaku*, **36**, 295 (1968).

5) K. Mucker, G. S. Smith, Q. Johnson, and R. E. Elson, *Acta Crystallogr., Sect. B*, **25**, 2362 (1969).

6) Pauling has reported that for the Th^{4+}–Cl^- ionic distance, the Th^{4+} and Cl^- ion radii are 2.95 and 1.81 Å, respectively, so that the Th^{4+}–Cl^- bond may be considered strong with significant overlapping of the electron clouds. Hence, it is reasonable that this structure be assumed to be of tetrahedron type to a first approximation. See, for example, L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, New York (1960), p. 518.

7) B. Gilbert, K. W. Fung, and G. Mamantov, *J. Inorg. Nucl. Chem.*, **37**, 921 (1975).

8) V. G. Keramidas and W. B. White, *J. Chem. Phys.*, **59**, 1561 (1973).

9) W. H. Zachariasen, *J. Am. Chem. Soc.*, **70**, 2147 (1948).

10) W. H. Zachariasen, *Acta Crystallogr.*, **7**, 792 (1954).