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RAMAN SPECTRA OF THE MOLTEN $MnCl_2$ - KCl SYSTEM

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The distribution of symmetric Mn - Cl stretching frequencies in molten $MnCl_2$ - KCl system was studied by laser-Raman spectroscopy. The stretching frequency was 208 cm^{-1} in pure $MnCl_2$ and 245 ∿ 251 cm^{-1} in KCl-rich compositions. The full width at half-height of Raman band increased with increasing $MnCl_2$ concentration from 38 cm^{-1} ($MnCl_2$: KCl = 1 : 4) to 110 cm^{-1} (pure $MnCl_2$).

Laser-Raman spectroscopy has been recently applied to study the formation of complex ions in a number of molten binary chloride systems. For instance, Maroni et al.[1] studied the $MgCl_2$ - KCl system and Clarke et al.[2] also studied the $CdCl_2$ - KCl system. They suggested that the tetrahedral complex ions, $MgCl_4^{2-}$ and $CdCl_4^{2-}$ exist dominantly in KCl-rich compositions in respective molten mixtures. Both pure $MnCl_2$ and $MgCl_2$ have a layer structure of $CdCl_2$-type in the solid phase, then in a certain sense molten $MnCl_2$ - KCl system is expected to have a similar structure as in the molten $MgCl_2$ - KCl or $CdCl_2$ - KCl system. However experimentally, the transition metal ion Mn^{2+} ($3d^5$) in melts has a certain optical absorption coefficient[3] in the visible region, and the intensity of Raman spectra of the system $MnCl_2$ - KCl is relatively smaller than that of $MgCl_2$ - KCl or $CdCl_2$ - KCl system.

The mixtures of $MnCl_2 \cdot 4H_2O$ and KCl of nine different compositions were put into a quartz test tube ($60 \times 8 \times 8 mm^3$). The tube was sealed off after evacuation with heating at about 200 °C for several hours. Raman spectra were recorded with a Shimazu Laser-Raman spectrophotometer (model R-2D, Shimazu Co.) equipped with 4880 A and 5145 A radiations from argon ion laser (Argon 165, Spectra Physics Co.) to excite the spectra. The 4880 A radiation was used for four specimens of mole fraction of $MnCl_2$, $x \leqq 0.4$ and the 5145 A radiation was used for five specimens of $x \geqq 0.5$ to raise the Raman intensity.

Fig.1(a) shows the Raman spectrum of the eutectic melt of LiCl - KCl (59-41 mole %) at 500°C by 4880 A radiation, which was used as a base line for assigning the spectra of $MnCl_2$ - KCl system.

Fig.1(b) shows the spectrum of solid $MnCl_2$ at 25°C by 4880 A radiation. There are four bands, peaked at 136, 172, 228 and 324 cm^{-1}. The band of 228 cm^{-1} is assigned to the symmetric Mn - Cl stretching band.[2] The full width at half-height (half-width), $\Delta\nu$ of the band of 228 cm^{-1} is about 7 cm^{-1}.

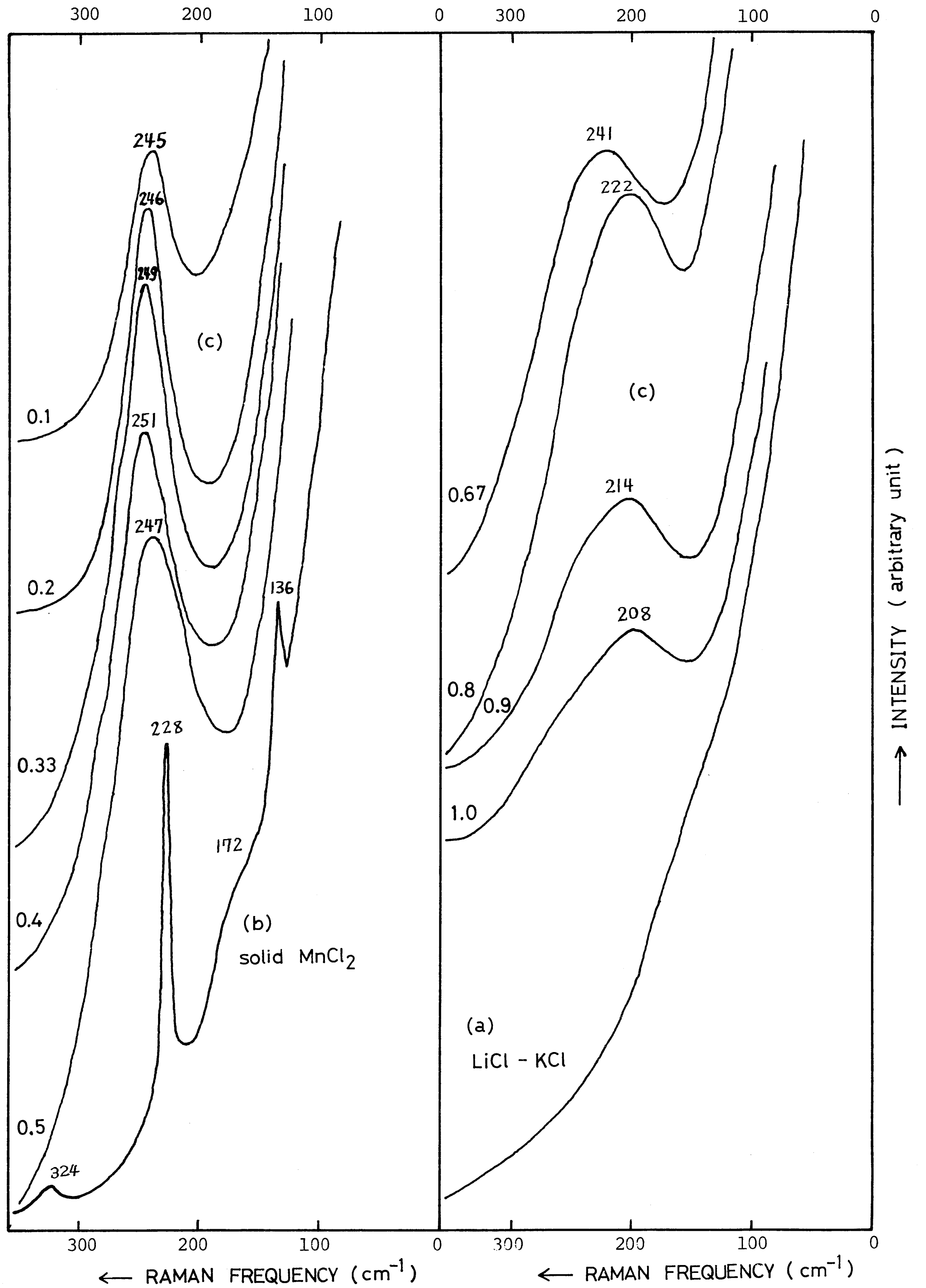

Fig.1 Raman spectra of (a) LiCl - KCl, (b) solid $MnCl_2$ and (c) $MnCl_2$ - KCl melts. Nine different values (0.1 ∿ 1.0) show the mole fraction of $MnCl_2$.

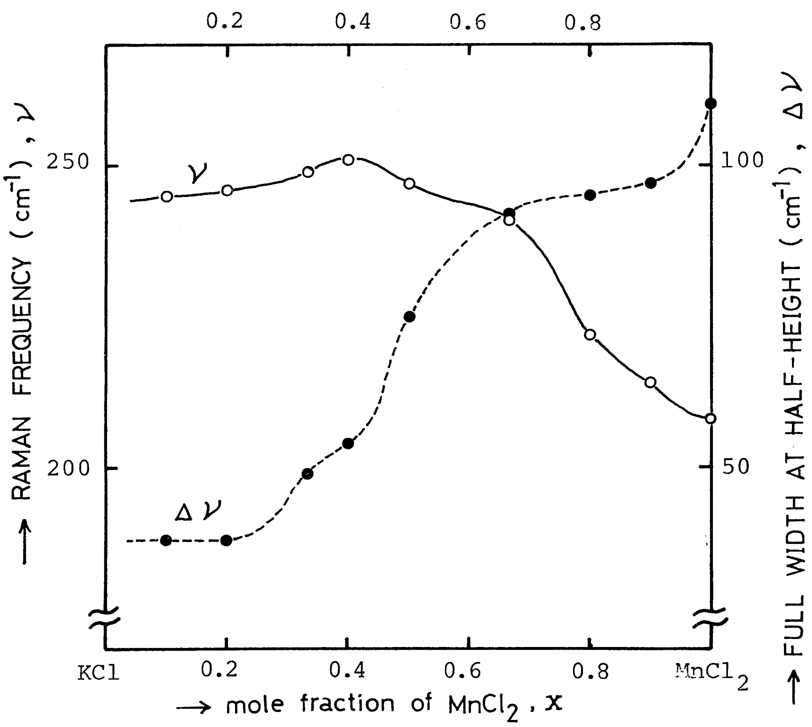

Fig.2 Behaviors of Raman frequency and full width at half-height against the mole fraction of $MnCl_2$.

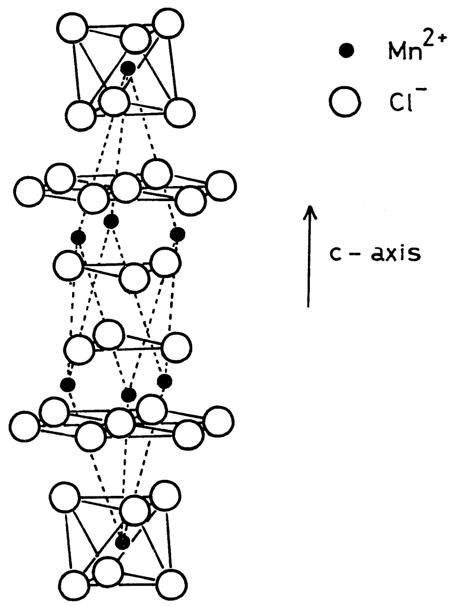

Fig.3 Crystalline $MnCl_2$-structure

Table 1. Observed values from the Raman spectra.

$x(MnCl_2)$	T (°C)	ν (cm^{-1})	Δν (cm^{-1})	Cl^-/Mn^{2+}
0.1	750	245	38	11
0.2	650	246	38	6
0.33	700	249	49	4
0.4	700	251	54	3.5
0.5	700	247	75	3
0.67	700	241	92	2.5
0.8	700	222	95	2.25
0.9	700	214	97	2.11
1.0	700	208	110	2

Curves in the Fig.1(c) show the spectra of various compositions of $MnCl_2$ - KCl melts at about 700°C. The intensity of each spectrum is not unified in a common scale. Only one band is observed in the range from 100 cm^{-1} to 400 cm^{-1} for every specimen. Each band was found to be the totally symmetric Mn - Cl stretching band[1), 2)] by insertion of a polarizer, and the other vibrational frequencies have not been observed because of their low intensity and a limited sensitivity of the spectrophotometer. The broad Raman scattering, peaked at 208 cm^{-1} is observed for pure $MnCl_2$. The frequency increases with increasing KCl content from 208 cm^{-1} for pure $MnCl_2$ to 251 cm^{-1} for the specimen of x=0.4, then it slightly decreases to 245 cm^{-1} for the specimen of x=0.1. These behaviors of Raman frequency ν are shown in Fig.2 and

Table 1. with half-width Δν of each Raman band against the composition. The half-width decreases with increasing KCl content from 110 cm^{-1} (pure $MnCl_2$) to 38 cm^{-1} (x=0.1 and x=0.2). These behaviors of ν and Δν may be discussed as follows.

The crystalline $MnCl_2$ has a layer structure consisting of repeat of one Mn^{2+}-layer and two Cl^--layers perpendicular to the c - axis as shown in Fig.3. Neighboring two Cl^--layers will be weakly bound each other in solid state. At the melting point (650°C) this weak bond between two Cl^--layers breaks. However, the bonds of Mn^{2+}-layer with the upper and lower Cl^--layers would not perfectly break, and there will remain species of $(MnCl_2)_n$ which have relatively large size above the melting point.[1] In these species $(MnCl_2)_n$, each Mn^{2+} ion may be octahedrally coordinated by six Cl^- ions and each Cl^- ion may be shared by Mn^{2+} ions. According to the addition of KCl to $MnCl_2$, the frequency ν increases to 214 cm^{-1} for the specimen of x=0.9 and it increases further to 222 cm^{-1} for the specimen of x=0.8 as shown in Fig.2. This increment of ν may correspond to the dissociation of the $(MnCl_2)_n$ species. That is, in addition of KCl to $MnCl_2$, $(MnCl_2)_n$ species are probably cut by the field strength of K^+ ions and the increment of the number of new Cl^- ions. Then each unit of $MnCl_6^{4-}$ octahedron seems to relatively isolate each other in comparison with that in pure $MnCl_2$, and the Raman frequency increases according to the increment of the force constant of Mn - Cl bond. The slight shoulder at ν ∿ 250 cm^{-1} in the spectra of the specimens, x=1.0, 0.9 and 0.8 (Fig.1(c)) will suggest the exsistence of a little amount of the another type of complex ions, such as $MnCl_4^{2-}$, as we discussed in a later section. While,in the composition region near KCl (x=0.1 and x=0.2) the band at ν ∿ 245 cm^{-1} has observed. This band can be assigned to the stretching frequency of the Mn - Cl bond of almost isolated tetrahedral $MnCl_4^{2-}$ complex ion.[1),2),3),4)] The formation of tetrahedral complex ion of MCl_4^{2-} - type has been proposed by many workers[3),4)] in the number of molten binary chloride systems. Sundheim et al.[3)] suggested that the tetrahedral $MnCl_4^{2-}$ ion predominates in dilute $MnCl_2$ solution in LiCl - KCl eutectic melt by the optical absorption. Papatheodorou et al.[4)] also suggested such results as above by the calorimetric investigation for the system $MnCl_2$ - ACl (A=K, Rb, Cs).

As shown in Fig.2, the Raman frequency ν slightly increases in the composition range of x=0.1 to x=0.4. This increment seems to be correspond to the possibility of new formation of another type of complex ion, such as $MnCl_3^-$ (pyramidal)[2)] or $Mn_2Cl_7^{3-}$. However, the tetrahedral $MnCl_4^{2-}$ ions seem to still exist predominantly in these region (x=0.2, 0.3 and 0.4), because there are sufficient number of Cl^- ions to form the $MnCl_4^{2-}$ ions as denoted in the ratio Cl^-/Mn^{2+} (Table 1.). When the composition of $MnCl_2$ exceeds x=0.4, the Raman frequency ν decreases. Hence, the structure of the $MnCl_2$ - KCl melt is sure to change in the region from x=0.5 to x=1.0. Probably the ionic species seems to change from tetrahedral $MnCl_4^{2-}$ ion to more highly connected complex ion according to the share of Cl^- ion by Mn^{2+} ions, then in $MnCl_2$ - very rich compositions the association of some complex species occurs according to much lack of Cl^- ions.

While,the behavior of the half-width Δν is rather simple as shown in Fig.2. In the composition of x=0.1 or x=0.2, Raman band is very narrow and sharp (Δν=38 cm^{-1}). This narrow band will correspond to the existence of the isolated tetrahedral $MnCl_4^{2-}$ ion. When the composition of $MnCl_2$ exceeds x=0.4, Δν increases very rapidly. This rapid increment will be a response of the association of complex ions (mainly $MnCl_4^{2-}$). Then, Δν slowly increases from x=0.67 to x=0.9. In the $MnCl_2$ - rich compositions, there will be various type of sharing of Cl^- ion, resulting in a broad Raman band in the melt caused by a certain distribution of Mn - Cl stretching frequencies. Summarizing these behaviors of ν and Δν, the decrease in ν vs. x may be correspond to the change in the type of complex ion, for instance, from $MnCl_4^{2-}$ to $MnCl_6^{4-}$ ($0.67 \leqq x \leqq 1.0$), and the increment in Δν vs. x seems to be correspond to the sharing of Cl^- ion.

Fig.4 shows the results of Raman studies reported by Maroni et al.[1] ($MgCl_2$-KCl) and Clark et al.[2] ($CdCl_2$-KCl). Although their experimental points are few, the similar behavior of ν vs. composition is seen in these systems. These behavior suggest that the binary molten chloride system MCl_2 - KCl (M=Mg, Cd, Mn) have the similar molten structure corresponding to the same MCl_2 concentration.

The change in ν and Δν on melting of pure $MnCl_2$ are very drastic as shown in Fig.1(b) and (c). The peaked frequency ν changes from 228 cm^{-1} (solid) to 208 cm^{-1} (melt) and the half-width Δν changes from 7 cm^{-1} (solid) to 110 cm^{-1} (melt). The decrease of the Raman frequency on melting may be associated with the decrease of force constant of Mn - Cl bond, that is the increase of the distance of Mn - Cl bond. While, the large value of the half-width in melt may be directly correlated to the certain distribution of Mn - Cl stretching frequency in disordered melt structure. The very small value of Δν in solid is caused by the ordered solid ($CdCl_2$-type) structure.

Fig.5 shows the spectra of the melting specimen of x=0.33 at three different temperatures, 500°C, 600°C and 700°C. The Raman frequency ν decreases from 254 cm^{-1}(500°C) to 249 cm^{-1}(700°C) and the Raman intensity also gradually decreases according to raising temperature. These changes seems to be mainly attributed to the thermal expansion, that is the increase of the distance of Mn - Cl bond

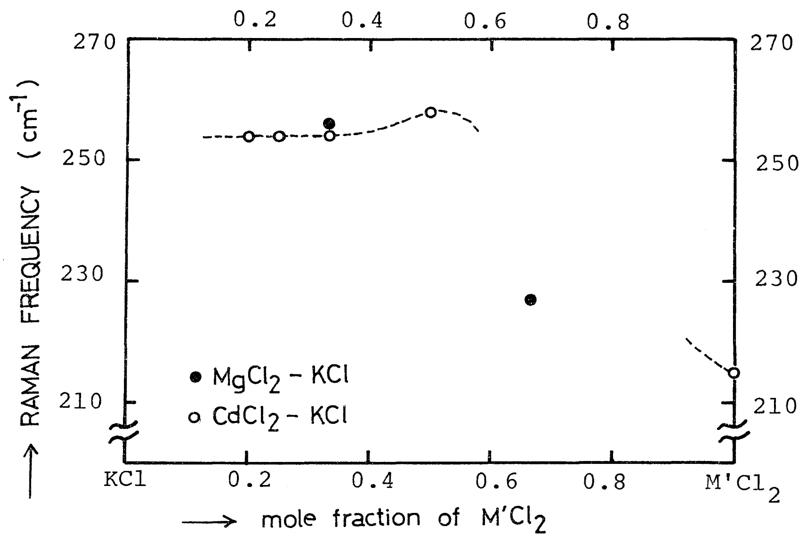

Fig.4 Raman frequency of the molten systems, $MgCl_2$ - KCl (Maroni et al.[1]) and $CdCl_2$ - KCl (Clarke et al.[2]).

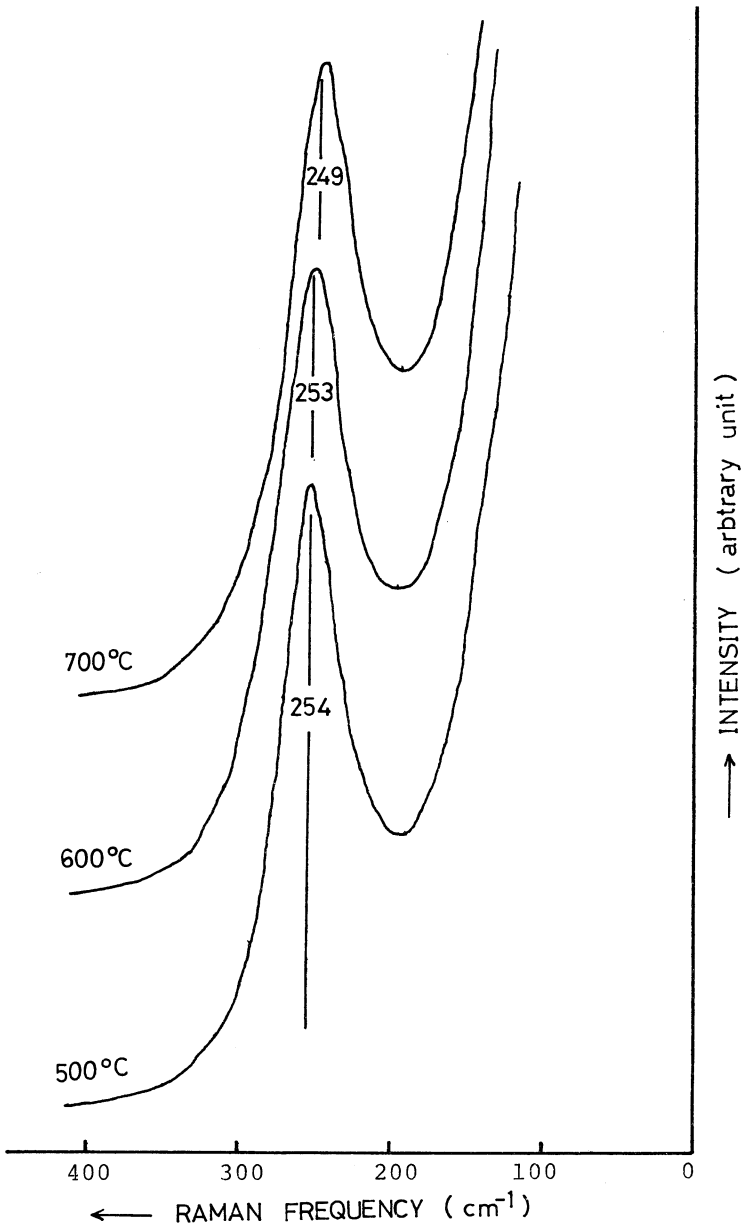

Fig.5 Temperature dependence of Raman band for the specimen, $MnCl_2$: KCl = 1 : 2.

according to the volume increase[5] with raising temperature. No prominent change in the half-width Δν was observed while the temperature was increased from 500°C (43 cm^{-1}) to 700°C (46 cm^{-1}).

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