^{113}Cd MAS and Static NMR Study of Chlorocadmate Glasses

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^{113}Cd magic-angle spinning (MAS) and static NMR spectra were measured of fourteen kinds of chlorocadmate glasses to reveal the chlorine coordination environments around Cd^{2+} in the glasses in detail. The spectra of the glasses suggest that the glass structures are mainly composed of infinite double-chains of edge-shared $CdCl_6$ octahedra, being independent of the $CdCl_2$ content and the kinds of chlorides except for $CdCl_2$. ^{113}Cd MAS and static NMR spectroscopies enabled us to reveal not only chlorine coordination number of Cd but also linkage manners between $CdCl_6$ octahedra in the glasses.

The structures of $CdCl_2$-based glasses have been investigated by means of Raman[1] and EXAFS[2] spectroscopies by Kadono et al. They have concluded that the chlorine coordination number of Cd^{2+} in these glasses is mainly five and six,[1] being close to six.[2] However, the more detailed information about the structures of $CdCl_2$-based glasses has not been obtained yet.

In the present study, ^{113}Cd MAS and static NMR spectra of chlorocadmate glasses are measured to reveal the chlorine coordination environments around Cd^{2+} in the glasses in detail. The chlorine coordination environments around Cd^{2+} in the glasses are discussed based on the relationship between NMR parameters such as isotropic chemical shift δ_{iso}, chemical shift anisotropy $\Delta\delta$ and asymmetry parameter η and the chlorine coordination environments around Cd^{2+}, which has been found in the ^{113}Cd MAS and static NMR study of chlorocadmate crystals.[3]

Chlorocadmate glasses of different compositions given in Table 1 were prepared. These glasses contained 0.7 mol% $NiCl_2$ in order to shorten the relaxation time of a Cd nucleus. Five-gram batches of well-mixed reagents were melted at 600–650 °C for 15 min in silica crucibles in a glove box filled with a dry Ar gas. Then the melts were quickly quenched by pressing them between a pair of brass plates in the glove box.

^{113}Cd MAS and static NMR spectra of powdered glasses were obtained at 88.738 MHz (9.4 T) with a Varian UNITY INOVA 400 MAS FT-NMR spectrometer. The acquisition parameters were a 4.0 µs pulse length, 1600–6400 scans and a 1.0–2.0 s pulse delays. Spinning rates were 5–6 kHz. Chemical shifts were referenced to a 1 M $Cd(ClO_4)_2$ aqueous solution at 0 ppm.

The principal components of the chemical shift tensors, δ_1, δ_2 and δ_3 can be estimated by fitting the theoretically calculated NMR spectra to the experimental NMR spectra. The detailed procedure has been described elsewhere.[4] The isotropic chemical shifts obtained from static NMR spectra ($\delta_{\mathrm{iso(static)}}$), $\Delta\delta$, and η can be also determined according to the following definitions:[5,6]

$$\delta_{\mathrm{iso(static)}} = (\delta_1 + \delta_2 + \delta_3)/3 \tag{1}$$

$$\Delta\delta = \delta_3 - [(\delta_1 + \delta_2)/2] \tag{2}$$

$$\eta = (\delta_2 - \delta_1)/(\delta_3 - \delta_{\mathrm{iso(static)}}) \tag{3}$$

The δ_1, δ_2, and δ_3 values can be determined based on Eq 4:

$$|\delta_3 - \delta_{\mathrm{iso(static)}}| \geq |\delta_1 - \delta_{\mathrm{iso(static)}}| \geq |\delta_2 - \delta_{\mathrm{iso(static)}}| \tag{4}$$

The absolute value of $\Delta\delta$ ($|\Delta\delta|$) reflects the degree of symmetry around a Cd atom, that is, symmetry around a Cd atom decreases with an increase of the $|\Delta\delta|$. The η reflects the degree of axial symmetry around a Cd atom; $\eta = 0$ for an axial symmetry around a Cd atom and $\eta = 1$ for an axial asymmetry.

Table 1. Isotropic chemical shifts ($\delta_{\mathrm{iso(MAS)}}$ and $\delta_{\mathrm{iso(static)}}$) determined by ^{113}Cd MAS and static NMR at 9.4 T, respectively, and chemical shift tensors (δ_1, δ_2, and δ_3), chemical shift anisotropy ($\Delta\delta$), and asymmetry parameter (η), determined by ^{113}Cd static NMR

Glass composition	$\delta_{\mathrm{iso(MAS)}}$	$\delta_{\mathrm{iso(static)}}$	δ_1	δ_2	δ_3	$\Delta\delta$	η
$40CdCl_2 \cdot 15NaCl \cdot 45BaCl_2$	199	199	88	191	319	180	0.86
$40CdCl_2 \cdot 20NaCl \cdot 40BaCl_2$	199	198	83	186	325	191	0.81
$40CdCl_2 \cdot 25NaCl \cdot 35BaCl_2$	185	188	92	174	297	164	0.75
$45CdCl_2 \cdot 20NaCl \cdot 35BaCl_2$	200	201	325	216	63	−208	0.79
$45CdCl_2 \cdot 20KCl \cdot 35BaCl_2$	205	205	95	196	325	180	0.84
$45CdCl_2 \cdot 10NaCl \cdot 10KCl \cdot 35BaCl_2$	199	200	98	191	312	168	0.82
$45CdCl_2 \cdot 20KCl \cdot 10SrCl_2 \cdot 25BaCl_2$	199	199	86	184	328	193	0.76
$50CdCl_2 \cdot 15NaCl \cdot 35BaCl_2$	198	197	300	210	80	−175	0.77
$50CdCl_2 \cdot 10KCl \cdot 40BaCl_2$	204	205	112	184	320	172	0.63
$50CdCl_2 \cdot 15KCl \cdot 35BaCl_2$	202	203	107	187	315	168	0.71
$50CdCl_2 \cdot 20KCl \cdot 30BaCl_2$	204	204	97	187	328	186	0.73
$50CdCl_2 \cdot 10KCl \cdot 5CsCl \cdot 35BaCl_2$	193	194	318	210	55	−209	0.78
$55CdCl_2 \cdot 15KCl \cdot 30BaCl_2$	203	203	85	192	333	195	0.82
$55CdCl_2 \cdot 20KCl \cdot 25BaCl_2$	201	202	92	185	330	192	0.73

All the values except for η have a unit of ppm. Experimental errors in $\delta_{\mathrm{iso(MAS)}}$ were within ±1 ppm. Experimental errors in $\delta_{\mathrm{iso(static)}}$, δ_1, δ_2, and δ_3 were within ±5 ppm.

Figure 1 shows the ^{113}Cd MAS and experimental and simulated static NMR spectra of $40CdCl_2{\cdot}25NaCl{\cdot}35BaCl_2$ glass as an example. The peak of MAS spectrum in the figure corresponds to the isotropic chemical shift obtained from MAS spectrum ($\delta_{iso(MAS)}$). The static spectrum is broader than the MAS spectrum. The simulated spectrum of $40CdCl_2{\cdot}25NaCl{\cdot}35BaCl_2$ glass satisfactorily reproduced the experimental spectra, supporting the validity of the calculated values of δ_1, δ_2, and δ_3. Thus, the δ_1, δ_2, and δ_3 values of all the glasses were estimated by fitting the simulated theoretical spectra to the experimental static spectra. Taking into account the very small difference between $\delta_{iso(MAS)}$ and $\delta_{iso(static)}$ (3 ppm at most), the values of δ_1, δ_2, and δ_3 obtained for all the glasses are presumed to be accurate. The determined δ_1, δ_2, and δ_3 values are summarized in Table 1. The $\delta_{iso(static)}$, $\Delta\delta$ and η values which were calculated from the δ_1, δ_2, and δ_3 values by using Eqs 1–3 are also listed in Table 1.

The $\delta_{iso(MAS)}$ values of the chlorocadmate glasses are plotted in Figure 2. These values are located in the $\delta_{iso(MAS)}$ range corresponding to linked $CdCl_6$ octahedra. This indicates that these glasses are comprised of linked $CdCl_6$ octahedra, that is, that Cd^{2+} in the glasses acts as a glass-forming cation.

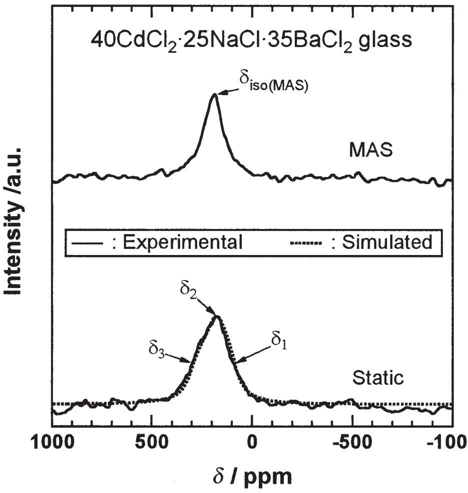

Figure 1. ^{113}Cd MAS and experimental and simulated static NMR spectra of $40CdCl_2{\cdot}25NaCl{\cdot}35BaCl_2$ glass.

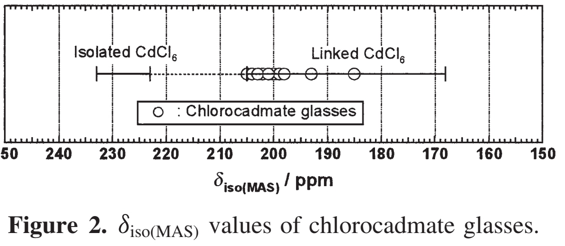

Figure 2. $\delta_{iso(MAS)}$ values of chlorocadmate glasses.

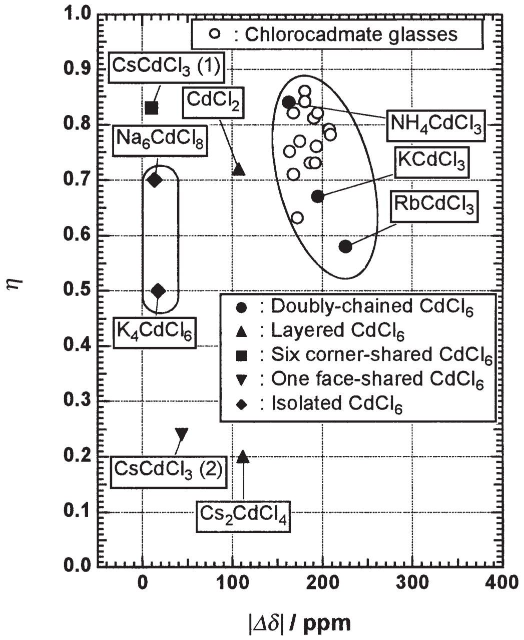

Figure 3. η–$|\Delta\delta|$ plot determined by ^{113}Cd static NMR of chlorocadmate glasses.

The $|\Delta\delta|$ and η values of the chlorocadmate glasses are plotted in Figure 3. The $|\Delta\delta|$ and η values are located in the region of doubly-chained $CdCl_6$ which means infinite double-chains of edge-shared $CdCl_6$ octahedra.[3] This result suggests that these glasses are mainly composed of infinite double-chains of edge-shared $CdCl_6$ octahedra and that the chlorine coordination environments around Cd^{2+} in the glasses are independent of the $CdCl_2$ content and the kinds of chlorides except for $CdCl_2$.

In the chlorocadmate glasses, ^{113}Cd MAS and static NMR spectroscopies enabled us to reveal not only chlorine coordination number of Cd but also linkage manners between $CdCl_6$ octahedra.

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