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MÖSSBAUER STUDY OF KCl-$ZnCl_2$-$FeCl_2$ GLASSES

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Mössbauer spectrum of xKCl·(90-x)$ZnCl_2$·10$FeCl_2$ glasses ($27 \geq x \geq 0$) suggests that Fe^{2+} ions are present, as a network modifier, at interstitial sites of the three-dimensional network composed of $ZnCl_4$ tetrahedra. A continuous decrease in the isomer shift observed with increasing KCl content is ascribed to the formation of nonbridging chlorine atoms at the neighboring sites of iron.

Structural studies of halide glasses are not so common as those of oxide glasses because of the difficulties in fabrication and because of the chemical instability or hygroscopic nature of some of these glasses. However, the halide glasses recently have been paid attention owing to the excellent optical transparency ranging from near UV to middle IR[1-3] and to the high fluoride ion conductivity observed in ZrF_4-based glasses.[4] Although more than half a century has passed since $ZnCl_2$ glass was first prepared,[5] the structure has not been completely understood. It is reported that binary $ZnCl_2$ glasses, such as KCl-, KBr-, and KI-$ZnCl_2$ glasses, are more stable than the pure $ZnCl_2$ glass.[6] Electronic, IR, and Raman studies of nickel(II)-doped $ZnCl_2$ glass[7] showed that the glass consists of a random network of $ZnCl_4$ tetrahedra similar to the structure of SiO_2 glass. The present work was performed to obtain the information on the structure of KCl-$ZnCl_2$-$FeCl_2$ glasses by means of Mössbauer spectroscopy which has been successfully used for the structural studies of several oxide glasses, such as borate,[8-11] borosilicate,[12,13] phosphate,[14,15] and borophosphate[16] glasses.

The KCl-$ZnCl_2$-$FeCl_2$ glasses were prepared in an electric furnace made for the purpose. The furnace is made of a transparent quartz tube (ø 80 mm) wound up with a Kanthal electrothermic wire. The quartz tube and the Kanthal wire are wrapped with asbestos to maintain the temperature. Each end of the tube is stoppered with a silicone rubber. Fusion of the mixture (0.2 g) of weighed quantities of KCl, $ZnCl_2$, and $FeCl_2$ was performed at 300 °C for 2 min in a stream of dry nitrogen to protect the melt from the atmospheric moisture and oxygen. All other procedures were also performed in a dry nitrogen atmosphere because $ZnCl_2$ is extremely hygroscopic. Transparent and almost colorless glasses were prepared by quenching the melts in platinum crucibles with ice-cold water in a beaker. Mössbauer measurements were performed by a constant acceleration method at room temperature using a source of ^{57}Co (5 mCi) diffused into a palladium foil. The velocity of spectrometer was calibrated with a metallic iron foil enriched with ^{57}Fe, which was also used as a reference for isomer shift. All the Mössbauer spectra were fitted to Lorenzian lineshapes by computer calculations.

The zinc chloride glasses prepared in the present study are expressed by a formula $xKCl\cdot(90-x)ZnCl_2\cdot10FeCl_2$, and the x value is changed from zero to 27 because the higher KCl content results in devitrification or phase separation. Mössbauer spectrum of these glasses consists of a quadrupole doublet with intensity lower than 1%. The weak absorption is explained by the low recoil-free fraction of the ^{57}Fe in the glasses, and also by a partial γ-ray absorption by zinc atoms. Mössbauer parameters for these glasses are summarized in Table 1, where the errors are estimated to be ± 0.02 mm s^{-1} for isomer shift and ± 0.10 mm s^{-1} or more for quadrupole splitting and linewidth. It is seen from Table 1 that iron is present as Fe^{2+} ions with octahedral symmetry because the isomer shifts exceed 1.0 mm s^{-1}.

Table 1. Mössbauer parameters for the $KCl-ZnCl_2-FeCl_2$ glasses

Glass	$\delta^{a)}$ / mm s^{-1}	$\Delta^{b)}$ / mm s^{-1}	$\Gamma^{c)}$ / mm s^{-1}
$90ZnCl_2\cdot10FeCl_2$	1.25	1.70	0.61
$4.5KCl\cdot85.5ZnCl_2\cdot10FeCl_2$	1.21	2.01	1.04
$9KCl\cdot81ZnCl_2\cdot10FeCl_2$	1.14	2.44	0.85
$13.5KCl\cdot76.5ZnCl_2\cdot10FeCl_2$	1.13	2.49	0.67
$18KCl\cdot72ZnCl_2\cdot10FeCl_2$	1.07	2.23	0.89
$27KCl\cdot63ZnCl_2\cdot10FeCl_2$	1.06	2.43	0.60

a) Isomer shift. b) Quadrupole splitting. c) Linewidth (FWHM).

(Isomer shifts for Fe^{2+} with octahedral and tetrahedral symmetries are in the ranges of 1.0–1.5 mm s^{-1} and 0.7–1.0 mm s^{-1}, respectively.[17]) Absorption due to Fe^{3+} is not observed in the present study. Isomer shift is also available for evaluating the nature of chemical bond between Mössbauer atom and the neighboring atoms, and it is generally known that the isomer shifts for ionically bonded iron are larger than those for covalently bonded iron. It is noteworthy that the isomer shifts for Fe^{2+} in $KCl-ZnCl_2-FeCl_2$ glasses (Table 1) decrease continuously with increasing KCl content. The decrease in the isomer shift, i.e. the increase in s-electron density at iron nucleus, means the increased covalency in the $Fe^{2+} - Cl^-$ chemical bond and also decreased Fe – Cl bond length.[18] The increase in the s-electron density at iron nucleus seems to reflect the formation of nonbridging chlorine atoms at the neighboring sites of iron, because the addition of alkali salt, i.e. KCl in the present study, is considered to produce network disruption.[19] This is well consistent with our previous results on several oxide glasses,[8,10-12] where continuous increases in the s-electron density at iron nucleus have been observed with the formation of nonbridging oxygen atoms. A drastic increase in the quadrupole splitting is also observed with the addition of KCl, i.e., the parameter is changed from 1.70 mm s^{-1} observed in the $90ZnCl_2 \cdot 10FeCl_2$ glass to 2.01–2.49 mm s^{-1} in the ternary $ZnCl_2$ glasses. The increased quadrupole splittings are ascribed to the decreased symmetry around iron nucleus owing to the incorporation of K^+ with larger ionic radius than that of Fe^{2+} into the binary $ZnCl_2-FeCl_2$ glass. These results are also supported by the increased linewidths observed in most of the ternary $ZnCl_2$ glasses containing KCl, because the increase in the linewidth corresponds to an increased complexity concerned with the Fe – Cl bond length and/or Cl – Fe – Cl bond angle.

These results lead to conclusions that Fe^{2+} ions in these glasses are present, as a network modifier, at interstitial sites of the three-dimensional network composed of $ZnCl_4$ tetrahedra, and that the chemical bond between Fe^{2+} and Cl^- becomes rather covalent when the fraction of KCl, which is also present as a network modifier, is high. The increased covalency is ascribed to the formation of nonbridging chlorine atoms at the neighboring sites of iron.

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