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MÖSSBAUER STUDY OF ZrF_4-BaF_2-FeF_3 GLASSES

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The Mössbauer spectra of ZrF_4-BaF_2-FeF_3 glasses revealed that both Fe^{2+} and Fe^{3+} with octahedral F coordination are present in the glasses. The compositional dependence of $Fe^{2+}/(Fe^{2+} + Fe^{3+})$, explainable with the basicity of glass, suggests that Fe^{2+} and Fe^{3+} behave like a glass modifier and a glass former, respectively.

ZrF_4-based glasses, discovered by Poulain et al. in 1975,1) are a new family of glasses and have such characteristics as chemical resistance to fluoridating agents, high fluorine-ion conductivity, and transparency from the near UV to the middle IR.2)

A mother glass for the ZrF_4-based glass systems is ZrF_4-BaF_2 glass, into which a variety of metal fluorides can be incorporated.3) Among the metal fluorides, transition metal fluorides and rare earth fluorides are interesting additives in connection with the development of optical and magnetic materials. The absorption and emission spectra characteristics of rare earth ions in the ZrF_4-based glasses have been intensively studied so far.2,4) On the contrary, little works have been done on transition metal-containing ZrF_4 glasses.5)

The characterization of iron fluoride in the ZrF_4-based glasses is very important and also very interesting; the iron ions at low concentrations are a coloring agent and an undesirable impurity in optical glass fiber and, on the other hand, those at high concentrations might induce semiconductive and/or ferromagnetic properties in glasses. Strangely, however, there is no study on ZrF_4-based glasses containing iron fluoride. Thus Mössbauer spectroscopic study was performed to examine the oxidation state, fluorine coordination environment, and structural role of iron ions in ZrF_4-BaF_2-FeF_3 glasses as the first stage of the study on iron-containing ZrF_4 glass.

The ZrF_4-BaF_2-FeF_3 glasses were prepared from 99% ZrF_4, reagent grade BaF_2, and 99.9% $FeF_3 \cdot 3H_2O$. About 5 g batches of the raw materials with addition of small amounts of NH_4HF_2 were melted in platinum crucibles in an N_2 gas atmosphere and kept at 1050 °C for 15 min. Then the melts were rapidly quenched by a twin roller. Thin filmy glasses of about 20 μm thickness were obtained. No inclusion of crystalline phases in the glasses was ascertained by X-ray diffraction. The batch compositions of six glasses prepared are given in Table 1. The glasses may be grouped into three series; series A (glasses 2, 3, and 4), series B (glasses 1, 4, and 6),

Table 1. Compositions of ZrF_4-BaF_2-FeF_3 glasses prepared, and Mössbauer parameter and [$Fe^{2+}/(Fe^{2+} + Fe^{3+})$] values observed for the glasses

Glass No.	Batch composition	Fe^{2+} IS/ $mm \cdot s^{-1}$	Fe^{2+} QS/ $mm \cdot s^{-1}$	Fe^{2+} Γ/ $mm \cdot s^{-1}$	Fe^{3+} IS/ $mm \cdot s^{-1}$	Fe^{3+} QS/ $mm \cdot s^{-1}$	Fe^{3+} Γ/ $mm \cdot s^{-1}$	$\left(\frac{Fe^{2+}}{Fe^{2+}+Fe^{3+}}\right)$/%
1	$40ZrF_4 \cdot 24BaF_2 \cdot 36FeF_3$	1.22	2.48	0.75	0.51	0.65	0.57	43
2	50 " ·40 " ·10 "	1.22	2.49	0.70	0.40	0.50	0.85	37
3	50 " ·30 " ·20 "	1.29	2.37	0.62	0.48	0.56	0.64	48
4	50 " ·20 " ·30 "	1.29	2.35	0.72	0.49	0.44	0.68	60
5	56 " ·34 " ·10 "	1.24	2.48	0.70	0.45	0.50	0.65	47
6	65 " ·14 " ·21 "	1.29	2.35	0.63	0.51	0.58	0.62	61
	crystalline FeF_2 6)	1.31	2.68	0.46				
	crystalline $(H_2O)_{0.33}FeF_3$ 7)				0.439	0.640	0.50	

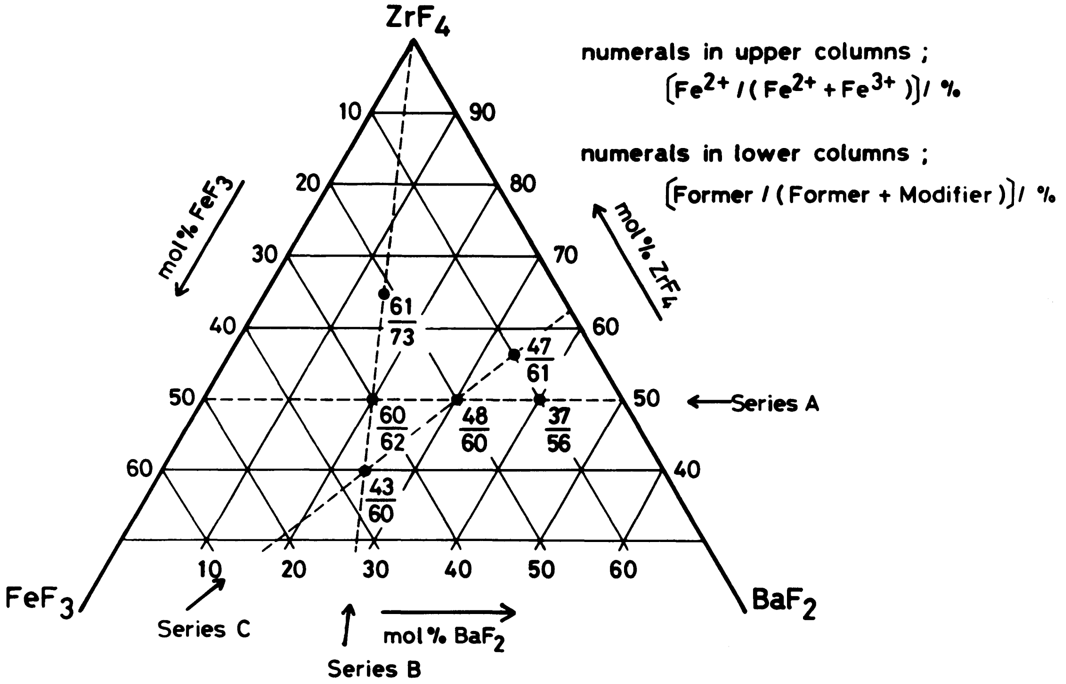

Fig. 1. Location of the present glasses, and compositional dependences of [$Fe^{2+}/(Fe^{2+} + Fe^{3+})$] (numerals in upper columns) and [glass-former/(glass-former + glass-modifier)] (numerals in lower columns).

and series C (glasses 1, 3, and 5). The location of the glasses in the ternary ZrF_4-BaF_2-FeF_3 diagram is shown in Fig. 1.

The Mössbauer measurements were made with a commercial TMC set (Gammascope 102, Drive unit 306, Transducer 305, Gamma Scientific Inc.) at room temperature. ^{57}Co doped in Cu metal and a proportional counter were used as the γ-ray source and the γ-ray detector, respectively. The pure iron absorber spectrum was utilized to calibrate the velocity scale and also as the standard for calculating the isomer shift. The Mössbauer spectra observed for the present glasses are shown by dots in Fig. 2. Assuming that the experimental points of Mössbauer spectra lie on two pairs of quadrupole splitting curves given by Lorentzian-type functions, the best fitting was performed by a trial and error method using a microcomputer. The results are shown by both broken and full lines in Fig. 2. The Mössbauer parameters [isomer shift (IS), quadrupole splitting (QS), and line width (Γ)] calculated from the two pairs of quadrupole splitting curves are summarized in Table 1, where those reported for crystalline FeF_2 6) and $(H_2O)_{0.33}FeF_3$ 7) are also given for comparison. Based on the literatures on Mössbauer spectroscopy8) and the Mössbauer data on crystalline iron fluoride the followings can be deduced from the present results: One doublet with the IS values of 0.45-0.51 $mm \cdot s^{-1}$ and the QS values of 0.44-0.65 $mm \cdot s^{-1}$ is due to Fe^{3+} and the other with the IS values of 1.22-1.29 $mm \cdot s^{-1}$ and the QS values of 2.35-2.49 $mm \cdot s^{-1}$, due to Fe^{2+}, and both Fe^{3+} and Fe^{2+} ions are in the high spin state and are octahedrally coordinated by fluorine ions.

The $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ values for the respective glasses, calculated from the Mössbauer peak areas of Fe^{2+} and Fe^{3+}, are given in the last column of Table 1. The numerals in upper columns in Fig. 1 are these values. The compositional dependence of the $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ in Fig. 1 implies the followings: (i) The FeF_3 substitution of BaF_2 at a constant ZrF_4 content causes the Fe^{2+} concentration to increase (see series A). (ii) An increase in ZrF_4 content at a constant BaF_2/FeF_3 content ratio increases the Fe^{2+} concentration (see series B). (iii) At a constant

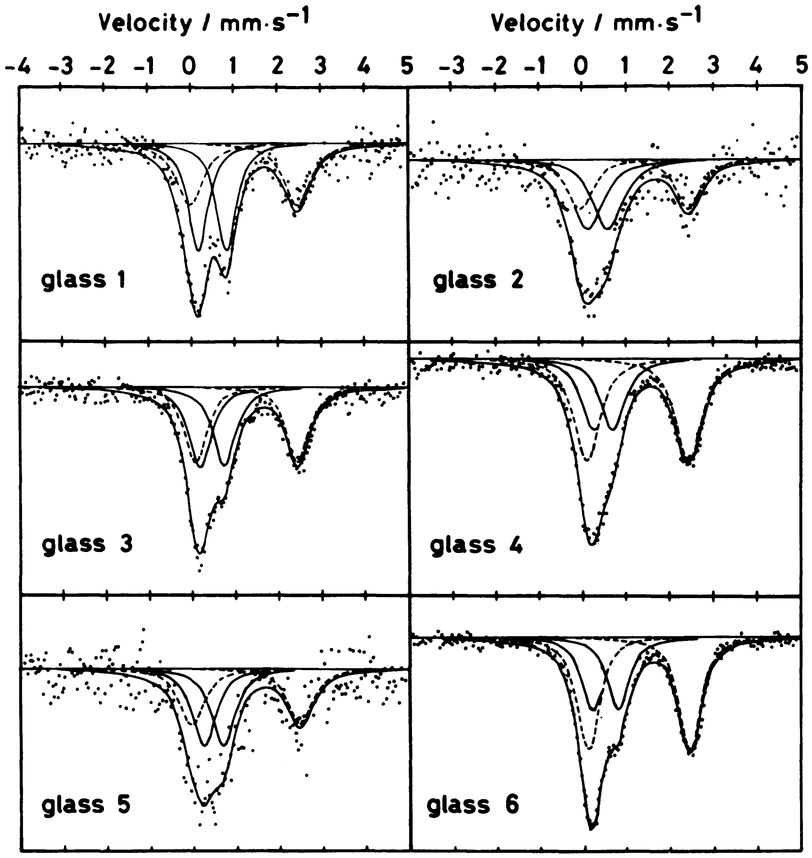

Fig. 2. Mössbauer spectra observed for ZrF_4-BaF_2-FeF_3 glasses.

BaF_2/ZrF_4 content ratio the $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ values vary little with FeF_3 content (see series C). Such variation of the $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratio with glass composition may be explained by the basicity of base glass. That is, an increase of the acidic ZrF_4 component in glass increases iron ions with low valence state, Fe^{2+}, and an increase of the basic BaF_2 component, iron ions with high valence state, Fe^{3+}. As discussed above, the Fe^{2+} and Fe^{3+} constitute $[Fe^{II}F_6]$ and $[Fe^{III}F_6]$ octahedra, respectively. When these two are compared, $[Fe^{III}F_6]$ is better as a glass former than $[Fe^{II}F_6]$. As an attempt the [glass-former/(glass-former + glass-modifier)] ratio was calculated for the respective glasses, assuming that the $[Fe^{III}F_6]$ and $[Fe^{II}F_6]$ are the glass-former and glass-modifier components, respectively. The numerals in lower columns in Fig. 1 are the values calculated from batch compositions. It can be seen that the values are roughly constant irrespective of glass composition. Thus it seems that, in fluoride glasses, the $[Fe^{II}F_6]$ and $[Fe^{III}F_6]$ octahedra behave like a glass modifier and a glass former, respectively.

In the Mössbauer study of sublimated FeF_3 films, Lachter et al. have reported the existence of tetrahedrally coordinated Fe^{3+} ions, of which the IS and QS values are 0.18-0.30 $mm \cdot s^{-1}$ and 0.31-0.40 $mm \cdot s^{-1}$, respectively.9) However no Mössbauer peak corresponding to such tetrahedrally coordinated Fe^{3+} ions could be found in the present glasses.

Together with this work, the behavior of iron ions in PbF_2-, ZnF_2-, and AlF_3-based glasses was also studied by Mössbauer spectroscopy to examine the difference in iron behavior due to the change in glass-forming system. The result will be reported elsewhere.10)

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