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Mössbauer, Raman, and DTA Studies on the Structure of BaF_2-ZrF_4-FeF_2 Glasses

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Structural studies on the ternary BaF_2-ZrF_4-FeF_2 glasses have been performed to elucidate the local structure of the ZrF_4-based glasses which are known to be excellent in the optical transparency and the electric conductivity due to F^- ion. Mössbauer and Raman measurements reveal that iron (Fe^{2+} and Fe^{3+}) plays a structural role similar to that of Ba^{2+} ion surrounded by eight fluorine atoms at the interstitial site of one- or two-dimensional zigzag chains composed of ZrF_6 octahedra. Raman and DTA measurements reveal that the increase in the fraction of BaF_2 causes an increase in the coordination number of Zr from 6 to 7. Mössbauer measurements of $25BaF_2 \cdot 65ZrF_4 \cdot 10FeF_2$ glass at lower temperatures lead to a conclusion that the glass undergoes a phase transition at 225 ± 5K, of which structural change is easily reflected in the isomer shift, quadrupole splitting, and the absorption area. This is supported by the DTA measurement of the same sample at lower temperatures, *i.e.*, the DTA curve consists of two exothermic peaks and a wide endothermic peak observed at about 220—230 K and 180—210 K, respectively.

Zirconium tetrafluoride (ZrF_4)-based glasses discovered by Poulain *et al.*[1] have recently been paid much attention owing to the excellent optical transparency ranging from near UV to middle IR[2—5] and to the relatively high fluoride ion conductivity.[6] The former property makes the ZrF_4-based glasses good candidates for optical waveguide materials and laser windows. Another feature of the glasses lies in the chemical resistancy to fluoridating agents such as HF and F_2.[4] In contrast to the relatively well-studied physical properties of these glasses, the structure has not been well understood. The structure of BaF_2-ZrF_4 glass system was studied by Almeida and Mackenzie[7] by means of IR and Raman spectroscopy. They obtained a conclusion that the structure consists of a two-dimensional zigzag chain in which each zirconium atom is surrounded by six fluorine atoms in octahedral symmetry when the BaF_2 content is not high. The coordination number of Zr has also been reported to be seven when the BaF_2 content is about 50 mol%. A similar conclusion was also obtained by Almeida and Mackenzie in a series of BaF_2- ZrF_2Cl_2 glasses.[8] X-Ray scattering studies of the BaF_2-ZrF_4 glass system was first performed by Coupê *et al.*,[9] and they obtained a conclusion that the glasses consist of three-dimensional network and that the coordination number of Zr is seven or eight. The present study was carried out to know the structure of BaF_2-ZrF_4-FeF_2 glasses by means of Raman spectroscopy, DTA, and Mössbauer spectroscopy which has been used for the structural studies of several glasses, such as borate,[10—12] borosilicate,[13,14] phosphate,[15,16] borophosphate,[17] germanate,[18] and zinc chloride[19] glasses.

Experimental

A series of ZrF_4-based glasses were prepared by fusing individual batches (1.0 g) of BaF_2 (99.9%), ZrF_4 (99.9%), FeF_2 (99.5%), and NH_4F (99.5%) in platinum crucibles at 900 °C for 3—5 min in an electric muffle furnace. Transparent and brown glasses were prepared by quenching the melts in the platinum crucibles with ice-cold water. Mössbauer measurements were performed by a constant acceleration method at various temperatures lower than room temperature using a source of ^{57}Co (10 mCi) diffused into a palladium foil. Metallic iron enriched with ^{57}Fe was used to calibrate the velocity of spectrometer and also as a reference for isomer shift. All the Mössbauer spectra were fitted to Lorenzian lineshapes by the least-squares method. Raman measurements were performed in the 90° scattering configuration at room temperature using a 514.5 nm Ar^+ laser line

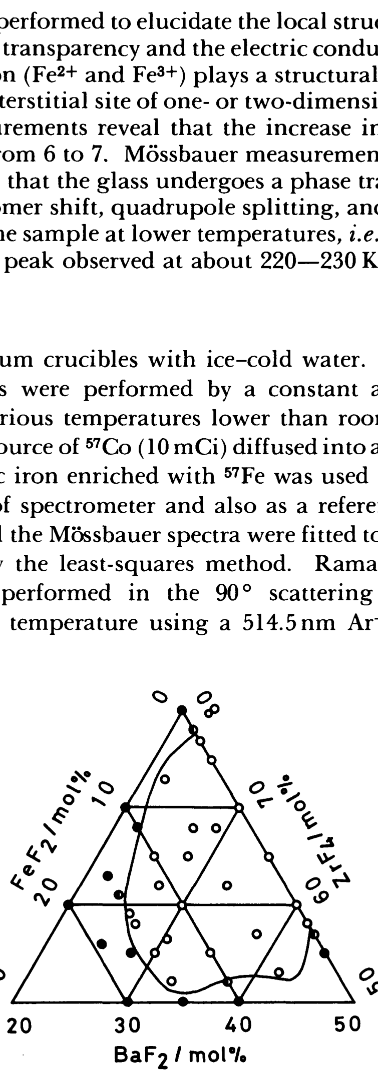

Fig. 1. Glass-forming region for the BaF_2-ZrF_4-FeF_2 system.
(○): Glass, (◐): glass ceramic, (●): crystalline compound.

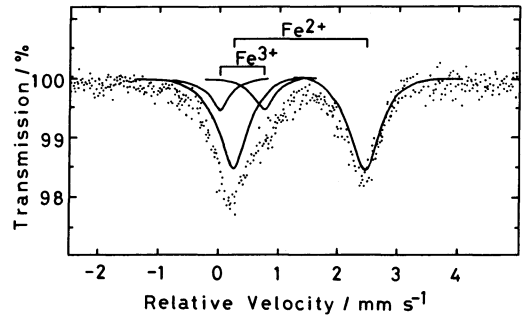

Fig. 2. Mössbauer spectrum for the $25BaF_2 \cdot 65ZrF_4 \cdot 10FeF_2$ glass measured at room temperature.

Table 1. Mössbauer and DTA results for the BaF_2-ZrF_4-FeF_2 glasses

Composition	$\delta^{a)}$	$\Delta^{b)}$	$\Gamma^{c)}$	$A^{d)}$	$T_g^{e)}$	$T_c^{f)}$
	$mm\,s^{-1}$	$mm\,s^{-1}$	$mm\,s^{-1}$	%	°C	°C
$25BaF_2 \cdot 65ZrF_4 \cdot 10FeF_2$	1.35	2.20	0.58	77.4	283	322
	0.40	0.73	0.49	22.6		
$30BaF_2 \cdot 60ZrF_4 \cdot 10FeF_2$	1.39	2.19	0.55	53.7	285	337
	0.41	0.95	0.61	46.3		
$35BaF_2 \cdot 55ZrF_4 \cdot 10FeF_2$	1.33	2.19	0.53	43.7	288	343
	0.37	0.86	0.70	56.3		

a) Isomer shift. b) Quadrupole splitting. c) Linewidth. d) Absorption area. e) Glass transition temperature. f) Crystallization temperature.

(100 mW). Slits were opened to 250 μm. Raman spectra were recorded in the HH (||) configuration where the scattered light was analyzed for the vector parallel to that of the incident radiation. DTA measurements of the glasses were performed with a heating rate of 5 °C min^{-1} ranging from −118 °C to 700 °C, and Al_2O_3 powder was used as a reference.

Results and Discussion

The composition region where glass samples were tried to prepare is shown in Fig. 1, in which open circles and closed circles refer to the formation of glass and crystalline sample, respectively and half-closed circles refer to glass ceramic. The glass-forming region of BaF_2–ZrF_4–FeF_2 system is denoted to lie within the area surrounded by a solid line. This is also expressed as 42 mol%$\geqslant BaF_2 \geqslant$22 mol%, 77 mol%$\geqslant ZrF_4 \geqslant$52 mol%, and 15 mol%$\geqslant FeF_2 \geqslant$0. Figure 1 also demonstrates that the glass-forming region of binary BaF_2–ZrF_4 glasses lies in 58—77 mol% ZrF_4, which is relatively well consistent with those reported by Almeida and Mackenzie (52—74 mol%),[7] Poulain *et al.* (60—70 mol%),[20] and Mitachi (58—69 mol%).[21] Mössbauer spectrum of $25BaF_2 \cdot 65ZrF_4 \cdot 10FeF_2$ glass measured at room temperature is shown in Fig. 2, from which we can estimate that most iron species are present as high-spin Fe^{2+} because the isomer shift is larger than 1.0 mm s^{-1}. Figure 2 also indicates that the spectrum contains a weak absorption due to Fe^{3+} of which isomer shift is *ca.* 0.4 mm s^{-1}. Mössbauer parameters for a few ZrF_4-based glasses are shown in Table 1 together with the results of DTA measurements. The errors are estimated to be ±0.01—0.02 mm s^{-1} for the isomer shift, ±0.02 mm s^{-1} or more for the quadrupole splitting and the linewidth, and ±0.5% for the absorption area. The errors are also estimated to be ±1 °C for the glass transition (T_g) and the crystallization (T_c) temperature. Large isomer shift values for Fe^{2+} suggest that each Fe^{2+} ion is surrounded by at least six fluorine atoms and that the chemical bond between iron and fluorine is extremely ionic,[22] because the isomer shift exceeds 1.3 mm s^{-1}. Isomer shift for Fe^{3+} suggests that each Fe^{3+} ion is also surrounded by at least six fluorine atoms. Quadrupole splitting and linewidth are typical of those for the absorption due to Fe^{2+} and Fe^{3+} in glasses. It seems that there is no systematic change in the Mössbauer parameters when the composition is changed. On the other hand, absorption area for the Fe^{2+} shows a distinct decrease with increasing BaF_2 content. This may be due to the increased oxidation atmosphere caused by the addition of BaF_2 into ZrF_4 matrix. (It is generally known that an increase in the basicity of glass matrix brought about by the increased alkali content, *i.e.*, BaF_2 content in the present study, results in an increase in the oxidation state of the transition metal ions in glasses. The present result is well consistent with this idea, and is also supported by the Mössbauer results recently reported by Kawamoto *et al.*[23]) It is also seen from Table 1 that T_g and T_c increase continuously with increasing BaF_2 content. The increase in T_g is also observed in binary BaF_2–ZrF_4 glasses,[7] in which a little higher (5—12 °C) T_g values are reported than those obtained in the present study. Glass transition temperature therefore seems to be reduced by the addition of FeF_2 into the BaF_2–ZrF_4 glasses. Considering that a very similar change in T_g has been observed in germanate glasses with a change in the coordination number of Ge(IV) from 4 to 6,[18] the continuous increases in T_g and T_c observed with the increasing fraction of BaF_2 (Table 1) are ascribed to a successive increase in the coordination number of Zr(IV). The change in the coordination number of Ge(IV) from 4 to 6 in the germanate glasses has also been confirmed by a continuous increase in a parameter of intermolecular force constant, $\theta^2 M$, obtained from the temperature dependence of the Mössbauer absorption area.[18] Low temperature measurements of the Mössbauer spectra were then carried out to obtain a structural information on BaF_2–ZrF_4–FeF_2 glasses. The parameter of intermolecular force constant ($\theta^2 M$) is known to be expressed by

$$\theta^2 M = \frac{3E^2}{kc^2}\left(\frac{-\,\mathrm{d}\ln f}{\mathrm{d}T}\right)^{-1}, \tag{1}$$

where E and f are Mössbauer transition energy (14.4 keV in the case of ^{57}Fe) and recoil-free fraction, respectively. In the Eq. 1, k is Boltzmann constant and c is the velocity of light. The $\theta^2 M$ value, in which θ is so-called Debye temperature and M is the mass of Mössbauer nucleus, can therefore be obtained from the slope of the

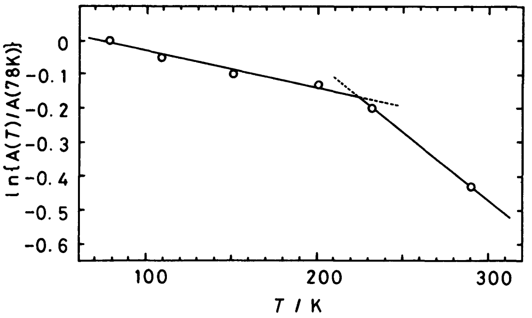

Fig. 3. Change in the absorption area (Fe^{2+} plus Fe^{3+}) with temperature.

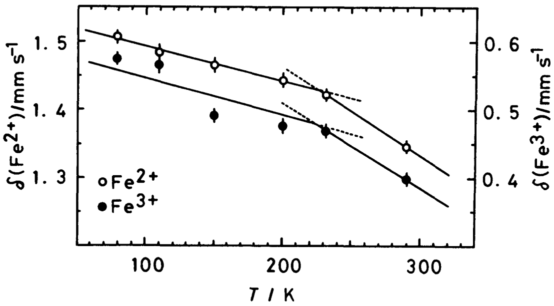

Fig. 4. Change in the isomer shifts of Fe^{2+} and Fe^{3+} with the temperature.

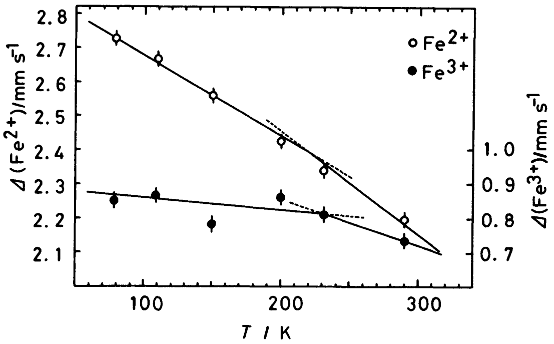

Fig. 5. Change in the quadrupole splittings of Fe^{2+} and Fe^{3+} with the temperature.

absorption area (A) *vs.* temperature (T) plot, because $d\ln f/dT$ can be approximated by $d\ln A/dT$ when a very thin sample is used. The results of the Mössbauer measurements at lower temperatures are shown in Figs. 3—5. The change in the absorption area with temperature is shown in Fig. 3, in which each absorption area is normalized by the area at 78 K. (Total absorption area for Fe^{2+} and Fe^{3+} is plotted in Fig. 3, because the separate plot for Fe^{2+} and Fe^{3+} also gives the same result as Fig. 3) It is obvious from Fig. 3 that the absorption area *vs.* temperature plot gives two straight lines with different slopes, and that the straight lines cross with each other at 224 K. The $\theta^2 M$ values obtained by dividing $3E^2/kc^2$, *i.e.*, 7.76×10^3 in the present study, with the slope of the individual straight line are 6.9×10^6 and 1.9×10^6 in the temperature ranges of 78—224 K and 224—290 K, respectively. The drastic change in the $\theta^2 M$ from 6.9×10^6 to 1.9×10^6 suggests that the intermolecular force between two Zr–F polyhedra is considerably weakened at 224 K, and that iron is present at relatively unstable environment in a sense of lattice dynamics. This leads to a tentative conclusion that iron is present at an interstitial site of Zr–F polyhedra rather than a substitutional site of Zr which is generally considered to be rigid. Large $\theta^2 M$ value (6.9×10^6) obtained in the temperature range of 78—224 K also supports the conclusion, suggesting that the nature of the chemical bond between iron and fluorine is essentially ionic because the $\theta^2 M$ values for the ionic compounds are known to be larger than those for the covalent ones ($1—3\times10^6$).[18] The $\theta^2 M$ value therefore seems to correspond to the intermolecular force between two zigzag chains composed of ZrF_6 octahedra.[7]

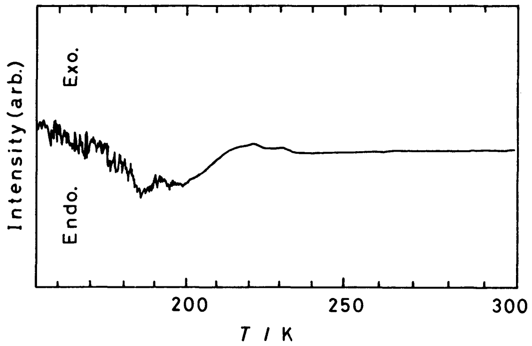

Fig. 6. DTA curve for the $25BaF_2\cdot65ZrF_4\cdot10FeF_2$ glass measured at 155—300 K.

The drastic change in the $\theta^2 M$ observed at 224 K also suggests that the $25BaF_2\cdot65ZrF_4\cdot10FeF_2$ glass undergoes a drastic change in the vibrational mode for some reason such as phase transition. Isomer shifts and quadrupole splittings for Fe^{2+} and Fe^{3+} at lower temperatures are shown in Figs. 4 and 5, and to our surprise these parameters also show distinct changes around 224 K, *i.e.*, at 225 K (isomer shift) and 220—230 K (quadrupole splitting). These Mössbauer results shown in Figs. 4 and 5 lead to a conclusion that a kind of structural change certainly occurs at 225±5 K in the $25BaF_2\cdot65ZrF_4\cdot10FeF_2$ glass, because the plots of isomer shift and quadrupole splitting *vs.* temperature are generally known to give rise to continuous curves similar to straight lines. DTA measurements at lower temperatures were then performed to confirm the structural change. Figure 6 demonstrates a DTA curve for the $25BaF_2\cdot65ZrF_4\cdot10FeF_2$ glass. It is obvious from Fig. 6 that an endothermic reaction occurs at 180—210 K, followed by an exothermic reaction observed around 220—230 K. The DTA curve suggests that a structural change (phase transition) certainly occurs around 225 K, and that the structural change spreads in such a wide region as can be detected by DTA method. It is therefore considered that a reorientation of

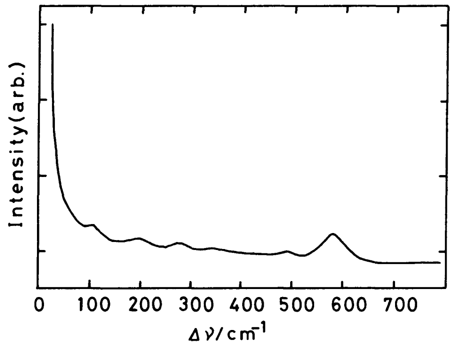

Fig. 7. Raman spectrum for the $30BaF_2 \cdot 60ZrF_4 \cdot 10FeF_2$ glass measured at room temperature.

several ions and atoms, similar to the crystallization at higher temperatures, occurs around 220—230 K.

Almeida and Mackenzie[7] revealed a mutual relationship between Raman peak position and the coordination number of Zr in binary BaF_2–ZrF_4 glasses by comparing each vibrational mode in glasses to that in the corresponding crystalline compounds. Polarized Raman spectrum of $30BaF_2 \cdot 60ZrF_4 \cdot 10FeF_2$ glass measured at room temperature is shown in Fig. 7. According to Almeida and Mackenzie,[7] a distinct peak observed around 580 cm^{-1} is assigned to the symmetric stretching vibrational mode (ν^s) due to four Zr-nonbridging fluorine (-F^-) bands in a ZrF_6 octahedron which constitutes one- or two-dimensional zigzag chain. A weak peak observed around 490 cm^{-1} has been assigned to a symmetric stretching vibration of bridging fluorine atom with which two ZrF_6 octahedra are linked together.[7] In the present study, the symmetric stretching vibrational mode (ν^s) due to the Zr–F^- band is observed at peak positions of 586, 580, and 572 cm^{-1} in $25BaF_2 \cdot 65ZrF_4 \cdot 10FeF_2$, $30BaF_2 \cdot 60ZrF_4 \cdot 10FeF_2$, and $35BaF_2 \cdot 55ZrF_4 \cdot 10FeF_2$ glasses, respectively. This continuous peak shift to the lower frequency region is ascribed to a gradual change in the coordination number of Zr from 6 to 7, because the peak position of the symmetric stretching vibrational mode (ν^s) for the Zr–F^- band is reported to be inversely correlated with the coordination number of Zr and because the peak is observed in the region of 570—600 cm^{-1} in the case of six-coordinated Zr.[7] Almeida and Mackenzie[7] also proved that the increasing fraction of BaF_2 causes a structural change from sheetlike (two-dimensional) zigzag chain to one-dimensional chainlike structure. We can therefore conjecture a structural role of FeF_2 in ZrF_4-based glasses by comparing the peak position of the symmetric stretching vibrational mode for the Zr–F^-band in the binary BaF_2–ZrF_4 glasses[7] with that in the ternary BaF_2–ZrF_4–FeF_2 glasses prepared in the present study. The Raman peaks due to the stretching vibrational mode (ν^s) have been observed at 598 and 580 cm^{-1} in the binary $25BaF_2 \cdot 75ZrF_4$ and $35BaF_2 \cdot 65ZrF_4$ glasses, respectively.[7] Comparison of these results with the peak position of $25BaF_2 \cdot 65ZrF_4 \cdot 10FeF_2$ glass (586 cm^{-1}) prepared in the present study leads to a conclusion that Fe^{2+} plays a structural role similar to that of Ba^{2+}, because the peak position of $25BaF_2 \cdot 65ZrF_4 \cdot 10FeF_2$ glass is almost identical with that of $35BaF_2 \cdot 65ZrF_4$ glass. A little increased peak position of $25BaF_2 \cdot 65ZrF_4 \cdot 10FeF_2$ glass compared to that of $35BaF_2 \cdot 65ZrF_4$ glass *i.e.*, 6 cm^{-1}, is ascribed to the displacement of Ba^{2+} with other metal ions of smaller ionic radii as is also found in the case of SrF_2–ZrF_4 glass.[7] Comparison of the peak position for the $30BaF_2 \cdot 60ZrF_4 \cdot 10FeF_2$ glass (580 cm^{-1}) with that of $40BaF_2 \cdot 60ZrF_4$ glass (577 cm^{-1}) also leads to the same conclusion as in the case of $25BaF_2 \cdot 65ZrF_4 \cdot 10FeF_2$ glass. This is also the case for the $35BaF_2 \cdot 55ZrF_4 \cdot 10FeF_2$ glass in which the corresponding peak (ν^s) is observed at 572 cm^{-1}. This peak position is intermediate between those of $40BaF_2 \cdot 60ZrF_4$ glass (577 cm^{-1}) and $50BaF_2$ $50ZrF_4$ glass (565 cm^{-1}). Coordination number of barium ion has already been reported to be in the range of 8—12 in several barium compounds,[9] and Ba^{2+} is known to be surrounded by eight fluorine atoms in BaF_2.[24] A barium ion is therefore assumed to be surrounded by eight fluorine atoms in one- or two-dimensional zigzag chains composed of ZrF_6 octahedra. The present results obtained from Raman and Mössbauer measurements therefore indicate that Fe^{2+} and Fe^{3+} ions are also surrounded by eight fluorine atoms. As for the coordination number of transition metal higher than six, some review articles[25–27] have been published, in which coordination number 8 is also observed in several metal compounds.

Peak intensity for the Zr–F^- stretching vibrational mode (ν^s) is also considered to give a useful information on the structural change based on the compositional change. In the present study, however, the peak intensity shows a maximum in the $30BaF_2 \cdot 60ZrF_2 \cdot 10FeF_2$ glass, contrary to our general expectation that the peak intensity will increase with increasing fraction of BaF_2. This can be attributed to the change in the coordination number of Zr from 6 to 7, and the fraction of nonbridging fluorine atoms (-F^-) will at least increase in the compositional region in which the coordination number of the central zirconium atom is invariable. Further experiments will be necessary to obtain a more detailed information on the fraction of nonbridging fluorine atoms in ZrF_4-based glasses.

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References

1) M. Poulain, M. Poulain, and J. Lucas, *Mater. Res. Bull.*, **10**, 243 (1975).

2) C. M. Baldwin, R. M. Almeida, and J. D. Mackenzie, *J. Non-Cryst. Solids*, **43**, 309 (1981).

3) L. G. Van Uitert and S. H. Wemple, *Appl. Phys. Lett.*, **33**, 57 (1978).

4) M. Poulain and J. Lucas, *Verres Refract.*, **32**, 505 (1978).

5) Y. Ohishi, S. Mitachi, T. Kanamori, and T. Manabe, *Phys. Chem. Glasses*, **24**, 135 (1983).

6) D. Leroy, J. Lucas, M. Poulain, and D. Ravaine, *Mater. Res. Bull.*, **13**, 1125 (1978).

7) R. M. Almeida and J. D. Mackenzie, *J. Chem. Phys.*, **74**, 5954 (1981).

8) R. M. Almeida and J. D. Mackenzie, *J. Non-Cryst. Solids*, **51**, 187 (1982).

9) R. Coupê, D. Louer, J. Lucas, and A. J. Leonard, *J. Am. Ceram. Soc.*, **66**, 523 (1983).

10) T. Nishida and Y. Takashima, *J. Non-Cryst. Solids*, **37**, 37 (1980).

11) T. Nishida, T. Shiotsuki, and Y. Takashima, *J. Non-Cryst. Solids*, **41**, 161 (1980).

12) T. Nishida, T. Hirai, and Y. Takashima, *J. Non-Cryst. Solids*, **43**, 221 (1981).

13) T. Nishida, T. Hirai, and Y. Takashima, *Phys. Chem. Glasses*, **22**, 94 (1981).

14) T. Nishida, T. Hirai, and Y. Takashima, *Bull. Chem. Soc. Jpn.*, **54**, 3735 (1981).

15) T. Nishida, T. Shiotsuki, and Y. Takashima, *J. Non-Cryst. Solids*, **43**, 115 (1981).

16) T. Nishida, T. Shiotsuki, and Y. Takashima, *J. Non-Cryst. Solids*, **43**, 123 (1981).

17) T. Nishida, Y. Miyamoto, and Y. Takashima, *Bull. Chem. Soc. Jpn.* **56**, 439 (1983).

18) T. Nishida, M. Katada, and Y. Takashima, *Bull. Chem. Soc. Jpn.*, **57**, 3566 (1984).

19) T. Nishida, A. Nakamura, and Y. Takashima, *Chem. Lett.*, **1984** 1683.

20) M. Poulain, M. Poulain, and J. Lucas, *Rev. Chim. Miner.*, **16**, 267 (1979).

21) S. Mitachi, *Phys. Chem. Glasses*, **23**, 190 (1982).

22) N. N. Greenwood and T. C. Gibb, "Mössbauer Spectroscopy," Chapman and Hall Ltd., London (1971), Chap. 5.

23) Y. Kawamoto, I. Nohara, K. Hirao, and N. Soga, *Solid State Commun.*, **51**, 769 (1984).

24) R. Mühll, S. Andersson, and J. Galy, *Acta Crystallogr., Sect. B*, **27**, 2345 (1981).

25) B. F. G. Johnson, "Transition Metal Chemistry," in "Comprehensive Inorganic Chemistry," ed by J. C. Bailar Jr., H. J. Emeleus, R. Nyholm, and A. F. Trotman-Dickerson," Pergamon Press, Oxford (1973), Vol. 4, Chap. 52.

26) E. L. Muetterties and C. M. Wright, *Quart. Rev.*, **21**, 109 (1967).

27) S. J. Lippard, *Prog. Inorg. Chem.*, **8**, 109 (1967).