154 © *1991 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 64, 154—160 (1991)* [Vol. 64, No. 1

Local Structure, T_g, and IR Transparency of Potassium Titanate Glasses and the Local Structure of Calcium Titanate Ceramics

Tetsuaki NISHIDA,* Yasuharu YAMAGUCHI, Miho YAMADA, and Yoshimasa TAKASHIMA
Department of Chemistry, Faculty of Science, Kyushu University,
Hakozaki, Higashiku, Fukuoka 812

(Received June 16, 1990)

The Mössbauer spectrum of $x\mathrm{K_2O}\cdot(95-x)\mathrm{TiO_2}\cdot5\mathrm{Fe_2O_3}$ glasses (x=35—60), consisting of a paramagnetic doublet peak due to tetrahedral $\mathrm{Fe^{3+}}$, suggests that the $\mathrm{Fe^{3+}}$ is substituted for the tetrahedral $\mathrm{Ti^{4+}}$. The isomer shift (δ=0.20—0.23 mm s^{-1}) and the quadrupole splitting (Δ=0.72—0.81 mm s^{-1}) decrease linearly with the increasing $\mathrm{K_2O}$ content. The glass transition temperature (T_g) decreases similarly as the Δ does, supporting the "T_g–Δ rule" discovered by Nishida et al., i.e., the T_g of oxide glasses is expressed by $T_g=a\Delta+b$. (The slope "a" is 680 °C mm^{-1} s.) The IR absorption spectra show two peaks at 880 and 640 cm^{-1} corresponding to the $\mathrm{Ti(Fe)O_4}$ and $\mathrm{TiO_6}$ units, respectively. The relative absorption intensity of the $\mathrm{Ti(Fe)O_4}$ units becomes higher when the $\mathrm{K_2O}$ content increases. The potassium titanate glasses (plate) show IR transparency, having the transmission edge of 5.4 μm. The Mössbauer spectrum of $x\mathrm{CaO}\cdot(95-x)\mathrm{TiO_2}\cdot5\mathrm{Fe_2O_3}$ ceramics (x=5—50) consists of two doublet peaks due to $\mathrm{Fe^{3+}}$ and $\mathrm{Fe^{2+}}$. Both the δ and Δ of the $\mathrm{Fe^{3+}}$ are constant irrespective of the CaO content, whereas the fraction (relative absorption area) of the $\mathrm{Fe^{3+}}$ decreases linearly from 94 to 75% when the CaO content is increased from 5 to 50 mol%.

It is known that $\mathrm{TiO_2}$-based (titanate) crystals such as $\mathrm{BaTiO_3}$ and $\mathrm{CaTiO_3}$ are excellent dielectric compounds. Titanate glasses are also known to have high dielectric constants and low thermal expansion coefficients. Structural study of the titanate glasses carried out by some groups revealed that $\mathrm{Ti^{4+}}$ ions are four- and six-fold coordinated with oxygen atoms.[1–3] In the IR and PAS (photoacoustic spectroscopy) study, Yoshimaru et al.[1] elucidated that the coordination number of $\mathrm{Ti^{4+}}$ depends on the basicity of the glass. Greegor et al.[4] reported that the coordination number of $\mathrm{Ti^{4+}}$ was four in the $\mathrm{TiO_2}$–$\mathrm{SiO_2}$ glass system, in which the $\mathrm{TiO_2}$ content was several mol%.

The Mössbauer spectroscopy is useful for the structural study of oxide glasses, because the Mössbauer ions (e. g. $\mathrm{Fe^{3+}}$) are easily substituted for the network forming ions (NWF) such as $\mathrm{Al^{3+}}$, $\mathrm{Ga^{3+}}$, $\mathrm{Te^{4+}}$, and $\mathrm{V^{5+}}$.[5–12] The present Mössbauer study was carried out in order to elucidate the coordination number of $\mathrm{Fe^{3+}}$ and $\mathrm{Ti^{4+}}$ in the $\mathrm{K_2O}$–$\mathrm{TiO_2}$ glasses and that in the CaO–$\mathrm{TiO_2}$ ceramics. Five mol% of $\mathrm{Fe_2O_3}$ is incorporated in these samples for the Mössbauer measurement. IR absorption measurement was carried out in order to elucidate the coordination number of $\mathrm{Ti^{4+}}$ and $\mathrm{Fe^{3+}}$ and also to confirm whether the $\mathrm{Fe^{3+}}$ is substituted for the $\mathrm{Ti^{4+}}$, as was done for the $\mathrm{Al^{3+}}$ in the study of calcium aluminate glass.[6] The IR transparency of the $\mathrm{K_2O}$–$\mathrm{Ti(Fe)O_2}$ glasses was found by measuring the IR spectrum of a piece of block (plate) sample. The other aim of this study is to confirm whether the "T_g–Δ rule", discovered by Nishida et al.[5] for several oxide glasses, holds for the titanate glasses.

Experimental

Potassium titanate glasses denoted by $x\mathrm{K_2O}\cdot(95-x)\mathrm{TiO_2}\cdot5\mathrm{Fe_2O_3}$ were prepared by melting individual mixtures (1 g) of commercially available $\mathrm{K_2CO_3}$, $\mathrm{TiO_2}$, and $\mathrm{Fe_2O_3}$ of guaranteed reagent grade. Each mixture in a platinum crucible was melted at 1400 °C for 2 h by use of an electric muffle furnace. After the fusion in air, each melt was quenched by quickly immersing the bottom of the platinum crucible into ice-cold water. As the result, brown glass samples could be obtained when the x was 35—60. Calcium titanate ceramics denoted by $x\mathrm{CaO}\cdot(95-x)\mathrm{TiO_2}\cdot5\mathrm{Fe_2O_3}$ were prepared by fusing individual mixtures (1 g) composed of $\mathrm{CaCO_3}$, $\mathrm{TiO_2}$, and $\mathrm{Fe_2O_3}$ at 1400 °C for 30 min. After the fusion, the melt was gradually cooled down to 150 °C. As the result, ceramic samples of reddish brown to gray color were obtained, depending on the CaO content. In the $x\mathrm{CaO}\cdot(95-x)\mathrm{TiO_2}\cdot5\mathrm{Fe_2O_3}$ system, no glass sample was prepared by the quenching procedure described above.

Mössbauer measurement was made on pulverized samples at room temperature by a constant acceleration method. Ten mCi (3.7×10^8 Bq) of cobalt-57 diffused into a palladium foil was used as the Mössbauer source. As the reference of the isomer shift (δ), a piece of metallic iron foil was used. The iron was also used for calibrating the velocity scale of the spectrometer. Each Mössbauer spectrum of the $x\mathrm{K_2O}\cdot(95-x)\mathrm{TiO_2}\cdot5\mathrm{Fe_2O_3}$ glasses was analyzed into a doublet peak having an equal linewidth by a least-squares method. In the case of $x\mathrm{CaO}\cdot(95-x)\mathrm{TiO_2}\cdot5\mathrm{Fe_2O_3}$ ceramic system, the Mössbauer spectrum was analyzed into two doublet peaks. DTA was conducted at the heating rate of 5 °C min^{-1}, ranging from room temperature to 900 °C. Alpha-$\mathrm{Al_2O_3}$ powder was used as the standard in the DTA measurements. IR absorption measurement was performed by the conventional KBr disk method, whereas the IR transmission measurement was made on the untreated $x\mathrm{K_2O}\cdot(95-x)\mathrm{TiO_2}\cdot5\mathrm{Fe_2O_3}$ glasses by use of a small block (plate) sample.

Results and Discussion

Potassium Titanate Glasses. The Mössbauer spectrum of potassium titanate glasses consists of a paramagnetic quadrupole doublet, as is illustrated in Fig. 1a. The quadrupole doublet indicates the presence of paramagnetic $\mathrm{Fe^{3+}}$ ions homogeneously

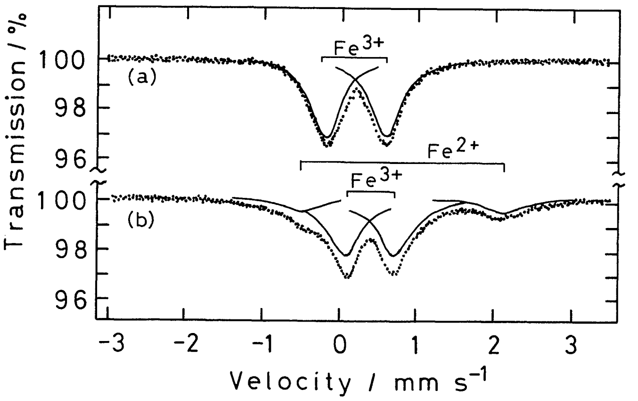

Fig. 1. The Mössbauer spectra of (a) $45K_2O \cdot 50TiO_2 \cdot 5Fe_2O_3$ glass and (b) $45CaO \cdot 50TiO_2 \cdot 5Fe_2O_3$ ceramic, measured at room temperature.

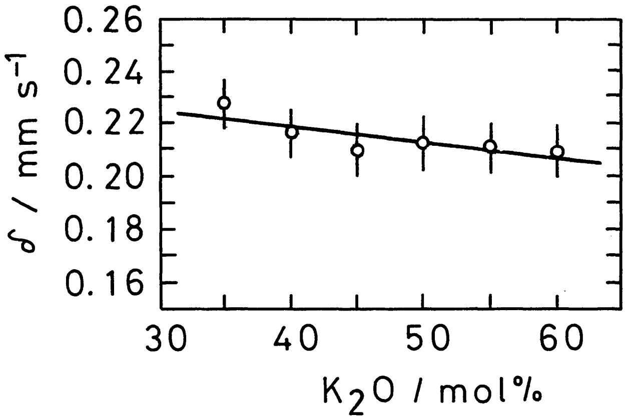

Fig. 2. The isomer shift (δ) for the $xK_2O \cdot (95-x)TiO_2 \cdot 5Fe_2O_3$ glasses plotted against the K_2O content.

distributed in the glass matrix; no magnetic species due to iron or iron oxide is observed. The isomer shift (δ), ranging from 0.20 to 0.23 mm s^{-1}, indicates the presence of tetrahedrally coordinated Fe^{3+} ions with oxygen atoms, as was observed for several oxide glasses.[5—10] The experimental error of the δ is estimated to be ±0.01 mm s^{-1}. The relatively small δ values reflect that the Fe^{3+}–O bond is fairly covalent. The compositional dependence of the δ is illustrated in Fig. 2, which shows a slight decrease when the K_2O content is increased from 35 to 60 mol%. A similar phenomenon has recently been observed in the Mössbauer studies of aluminate,[5] gallate,[5,7] and vanadate[8—10] glasses; the formation of nonbridging oxygen (NBO) causes the decrease of δ, corresponding to the increase of 4s-electron density at the nuclear site of iron, because the bond length of the Fe^{3+}–NBO bond is smaller than that of the Fe^{3+}–BO (bridging oxygen) bond. The coordination number of network former (NWF), i.e. Ti^{4+} in this study, can easily be known from the IR spectra.[13] Tarte reported that tetrahedrally and octahedrally coordinated Ti^{4+} have the IR absorption bands at 690—800 cm^{-1} and 500—650 cm^{-1}, respectively. The IR absorption spectra of the $xK_2O \cdot (95-x)TiO_2 \cdot 5Fe_2O_3$ glasses studied in this paper are shown in Fig. 3, together with the IR spectrum of α-Fe_2O_3 (Fig. 3g) used for the sample preparation. According to Tarte,[13] the absorption peaks observed at 880 and 640 cm^{-1} in Figs. 3a—f are ascribed to the tetrahedral and octahedral Ti^{4+}, respectively. Figures 3a—f shows a systematic change, i.e., the relative absorption intensity A_{tet}/A_{oct} increases with the increasing K_2O content. (The subscript "tet" and "oct" refer to the tetrahedral and octahedral Ti^{4+}, respectively.) Figure 3 indicates that the $xK_2O \cdot (95-x)TiO_2 \cdot 5Fe_2O_3$ glasses are composed of only the TiO_4 tetrahedra and the TiO_6 octahedra, and that no absorption peak due to Fe–O bond is observed. It is seen from Fig. 3 that the fraction of TiO_4 tetrahedra is increased at the expense of TiO_6 octahedra when the K_2O content is increased, as was observed in the case of iron-free titanate glasses.[1] These results suggest that the structural change occurring at the Fe^{3+} site is essentially the same as that occurring at the tetrahedral Ti^{4+} site, and that small amount (5 mol%) of Fe_2O_3 itself brings about no specific structural change in the

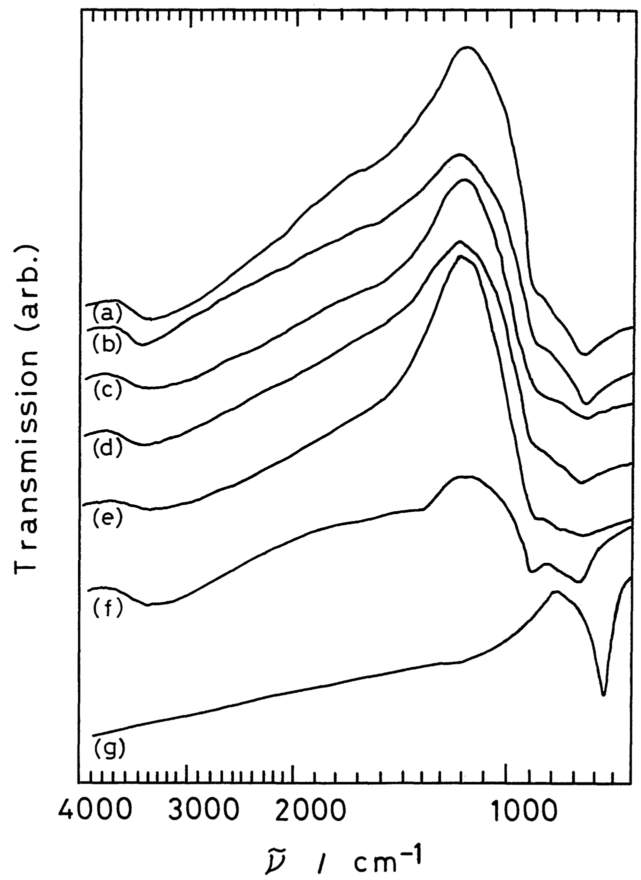

Fig. 3. The IR absorption spectra of $xK_2O \cdot (95-x)TiO_2 \cdot 5Fe_2O_3$ glasses; (a): x=35, (b): x=40, (c): x=45, (d): x=50, (e): x=55, (f): x=60. (g): The IR spectrum of Fe_2O_3.

K_2O–TiO_2 glasses. (We can obtain the structural information on the tetrahedral Ti^{4+} from the Mössbauer measurements.)

It is the characteristic feature of Figs. 3a—f that the Fe–O stretching vibration is not observed, whereas it was originally observed at 542 cm^{-1} in the IR spectrum of α-Fe_2O_3 (Fig. 3g). The absence of the Fe–O vibration suggests that no aggregate or precipitate of iron (Fe^{3+}) oxide is present in the $xK_2O\cdot(95-x)TiO_2\cdot 5Fe_2O_3$ glasses, and that the Fe^{3+} is vibrating at the substitutional site of the Ti^{4+}. In other words, the Fe^{3+} in the potassium titanate glasses seems to behave as if it were Ti^{4+} from the lattice vibrational point of view. It is noted that the Ti^{4+}/Fe^{3+} ratio is large, being in the range of 7—12 when the K_2O content is 35—60 mol%. The atomic substitution of Fe^{3+} for the NWF has also been confirmed in the case of Al^{3+}, which constitutes the network structure of calcium aluminate glass,6) i.e., only the stretching vibration due to the Al^{3+}–O bond was observed in the original aluminate glass having 5 mol% of Fe_2O_3. No characteristic vibration due to the Fe^{3+}–O bond was observed in the aluminate glass,6) whereas the corresponding vibration appeared as the crystallization (precipitation of $12CaO\cdot 7Al_2O_3$ phase) proceeded. In the present study, it is concluded that the Fe^{3+} ions are forming FeO_4 tetrahedra at the substitutional site of the TiO_4 tetrahedra, and therefore it is considered that the bond length of the Fe^{3+}–O bond is essentially the same as that of the Ti^{4+}–O bond. (The ionic radius of the Fe^{3+} (0.64 Å) is reported to be almost identical with that of the Ti^{4+} (0.68 Å).14))

The quadrupole splitting (Δ), corresponding to the difference in the energy level of nucleus ($I=3/2$) at the excited state, is expressed by

$$\Delta = (e^2qQ/2) \times (1 + \eta^2/3)^{1/2}, \qquad (1)$$

where eq and Q are the electric field gradient tensor ($=V_{zz}$) along the z-axis and the nuclear quadrupole moment, respectively.15) The η is an asymmetry parameter of the electric field gradient tensor, i.e., $(V_{xx}-V_{yy})/V_{zz}$.15) We can obtain useful information on the local distortion in the glasses, i.e., a deviation from the cubic symmetry of the NWF-oxygen polyhedra, since the Mössbauer ions (Fe^{3+} in this paper) are substituted for the NWF. Figure 4 demonstrates the compositional dependence of the Δ for Fe^{3+} in the $xK_2O\cdot(95-x)TiO_2\cdot 5Fe_2O_3$ glasses. The experimental error is estimated to be ±0.02 mm s^{-1}. The Δ shows a linear decrease with the increasing K_2O content, suggesting that the symmetry of FeO_4 tetrahedra becomes higher. This is also the case for the TiO_4 tetrahedra, because the FeO_4 tetrahedra are substituted for the TiO_4 tetrahedra, as described above. The decrease of the Δ (i.e. an increase of the symmetry) is ascribed to the formation of NBO in the Ti(Fe)O_4 tetrahedra, as was observed for the V(Fe)O_4 tetrahedra in the vanadate glasses.8—10) The formation of NBO in the present titanate glasses indicates the destruction of three-dimensional network structure composed of TiO_4 and TiO_6 octahedra.

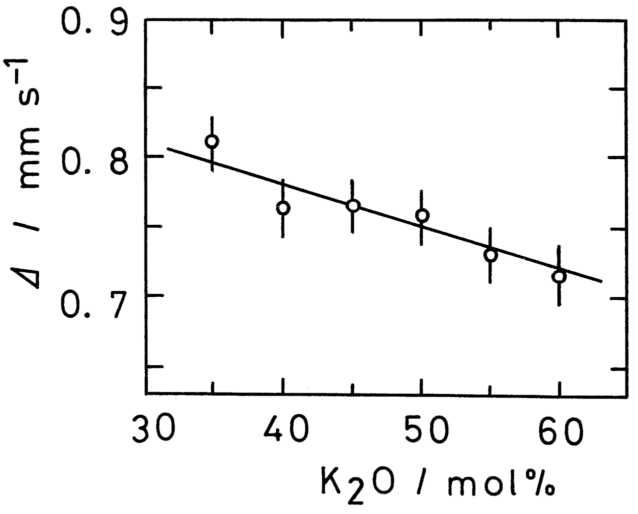

Fig. 4. The quadrupole splitting (Δ) for the $xK_2O\cdot(95-x)TiO_2\cdot 5Fe_2O_3$ glasses plotted against the K_2O content.

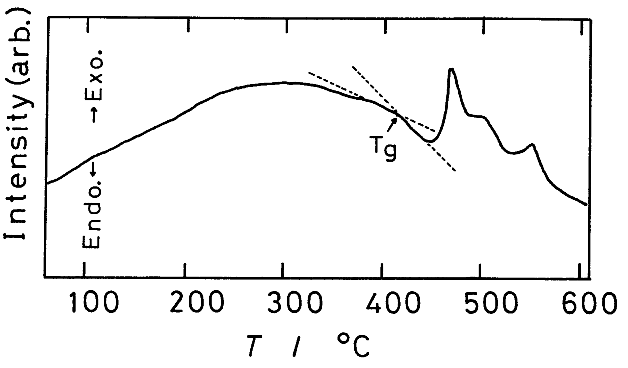

Fig. 5. A DTA curve of the $45K_2O\cdot 50TiO_2\cdot 5Fe_2O_3$ glass.

One of the DTA curve is shown in Fig. 5, in which the T_g is observed at about 415 °C. The compositional change of the T_g is illustrated in Fig. 6. The experimental error for the T_g is estimated to be ±1 °C. A linear decrease of the T_g from 436 to 398 °C, observed when the K_2O content is increased from 35 to 60 mol%, is consistent with the decrease of δ (Fig. 2) and that of Δ (Fig. 4), from which the formation of NBO was deduced. The decrease of the T_g ascribed to the formation of NBO suggests that the rotation of oxygen atoms becomes frequently at lower temperatures. The less complicated structure of the titanate glasses will be directly concerned with the lowering of the T_g.

The T_g obtained for the $xK_2O\cdot(95-x)TiO_2\cdot 5Fe_2O_3$ glasses is plotted against the Δ of Fe^{3+} (Fig. 7). It is seen from Fig. 7 that a linear relationship exists. The linear relationship ("T_g-Δ rule") has recently been discovered by Nishida et al.5) for several oxide glasses,

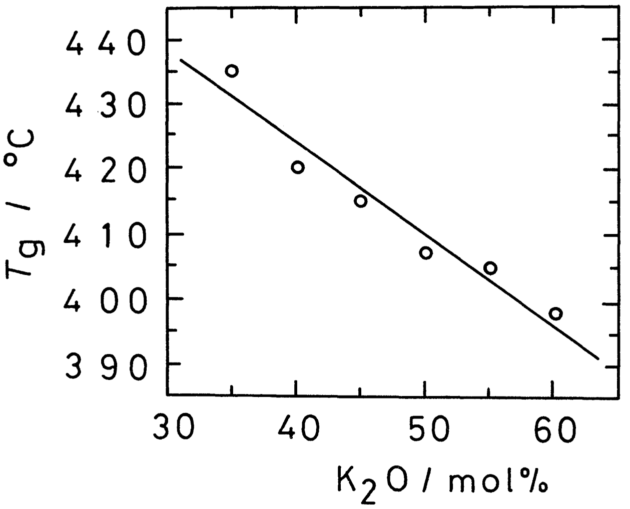

Fig. 6. The glass transition temperature (T_g) of xK$_2$O$\cdot$(95$-x$)TiO$_2\cdot$5Fe$_2$O$_3$ glasses plotted against the K$_2$O content.

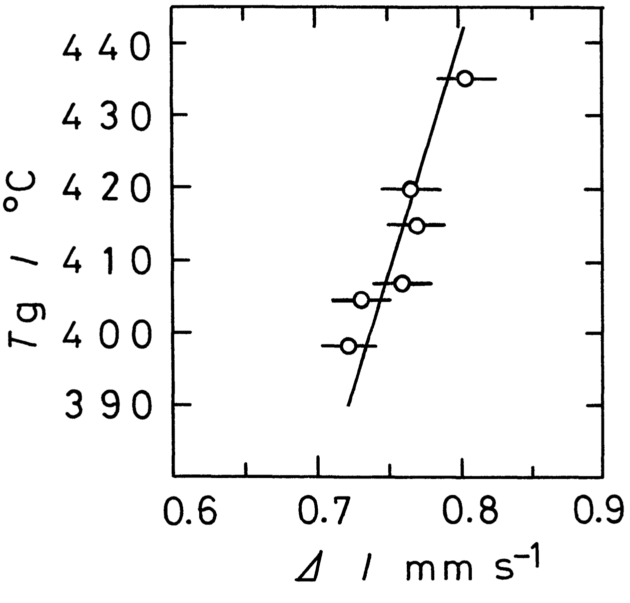

Fig. 7. The T_g-Δ plot for the xK$_2$O$\cdot$(95$-x$)TiO$_2\cdot$5Fe$_2$O$_3$ glasses.

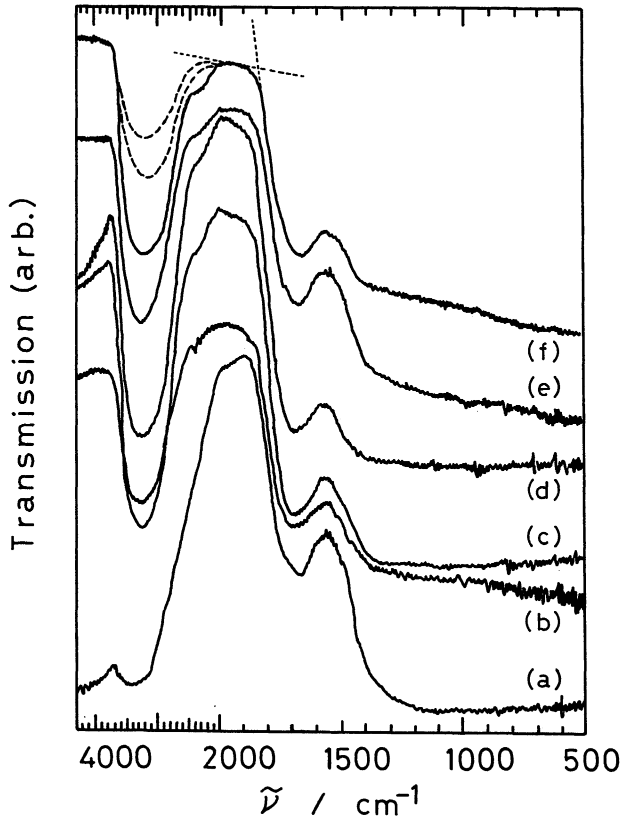

Fig. 8. The IR transmission spectra of the xK$_2$O$\cdot$(95$-x$)TiO$_2\cdot$5Fe$_2$O$_3$ glasses; (a): x=35, (b): x=40, (c): x=45, (d): x=50, (e): x=55, (f): x=60. The transmission edge is indicated by the intersection point of two straight lines (dotted line).

i.e., the T_g (°C) and the Δ (mm s^{-1}) can be expressed by the following equation,

$$T_g = a\Delta + b, \qquad (2)$$

where "a" is 680 °C mm^{-1} s and "b" is -180 °C ($\pm$100 °C) when the Fe^{3+} is present at the substitutional site of the NWF. The slope "a" of the straight line shown in Fig. 7 is estimated to be 680 °C mm^{-1} s and the intercept "b" is -100 °C, which is identical to that obtained for several oxide glasses, i.e. -180 °C,[5] if we take account of the experimental error of $\pm$100 °C. The "T_g-Δ rule" indicates that the T_g is closely concerned with the Δ, being proportional to the asymmetry of NWF (Ti^{4+} in this study)-oxygen polyhedra, i.e., to the local distortion of the network structure. It should be noted that the T_g is little related to the binding energy of the NWF–oxygen bond, as was discussed in Ref. 5.

A small block (plate) of the xK$_2$O$\cdot$(95$-x$)TiO$_2\cdot$5Fe$_2$O$_3$ glasses shows IR transparency, as is illustrated in Fig. 8. All the titanate glasses have the identical transmission edge of 5.4 μm (1850 cm^{-1}). The absorption edge is estimated to be about 7 μm (1400 cm^{-1}). The IR transparency, having the similar transmission edge as the present titanate glasses, is reported in the case of aluminate glasses with[16] and without[17] TiO$_2$ as well as gallate and tellurite glasses.[5] It seems that the highly optical transparency of the titanate glasses in the IR region is closely concerned with the noticeable local distortion and the large number of NBO atoms, similarly to the case of aluminate, gallate, and tellurite glasses.[5] The optical transparency in the IR region indicates that the titanate glasses can be a good candidate for the "optical memory" in the field of optoelectronics, in analogy with the aluminate, gallate, and tellurite glasses. We can utilize a change (usually a decrease) of the IR transmittance caused by the crystallization of the IR-transmitting glasses.

Figure 8 demonstrates an intense absorption due to the OH group around the wave number of 3 μm (3300 cm^{-1}). The absorption intensity due to the OH group is little changed by the heat treatment at 110 °C for 2 h, whereas it is reduced to ca. 63 and 45% by the treatment at 200 °C for 2 and 17 h, respectively. This is shown with broken lines in Fig. 8. These experimental results suggest that the OH group is not physically adsorbed on the surface of the glass sample, but is chemically bonded to the Ti^{4+} or Fe^{3+} constituting the network structure.

Calcium Titanate Ceramics. The Mössbauer spectrum of $45CaO \cdot 50TiO_2 \cdot 5Fe_2O_3$ ceramic is shown in Fig. 1b, which consists of a quadrupole doublet due to Fe^{3+} and a weak doublet due to Fe^{2+}. (Mössbauer measurements were performed in the velocity range of ±5.0 mm s^{-1}, and no magnetic species was observed.) All the Mössbauer spectra of $xCaO \cdot (95-x)TiO_2 \cdot 5Fe_2O_3$ ceramics consist of the two kinds of doublet peaks. The linewidth (Γ) of the doublet peaks is in the range of 0.36—0.60 mm s^{-1}, being almost comparable to that of several oxide glasses such as aluminate,[5,6] gallate,[5,7] vanadate,[8—10] and tellurite[11,12] glasses. It is seen from Fig. 1a and 1b that the Γ of $xCaO \cdot (95-x)TiO_2 \cdot 5Fe_2O_3$ ceramics is comparable to that of $xK_2O \cdot (95-x)TiO_2 \cdot 5Fe_2O_3$ glasses. This means that both the Fe^{3+} and Fe^{2+} are present in the glassy phase of the $xCaO \cdot (95-x)TiO_2 \cdot 5Fe_2O_3$ ceramics. They should be called glass-ceramics rather than ceramics. The formation of crystalline phase in the glass-ceramics was confirmed from the X-ray diffraction measurements. Figure 9 indicates the presence of TiO_2 phase precipitated in all the $xCaO \cdot (95-x)TiO_2 \cdot 5Fe_2O_3$ ceramic samples. Each diffraction peak corresponding to the TiO_2 phase is marked with an open circle in Fig. 9a.

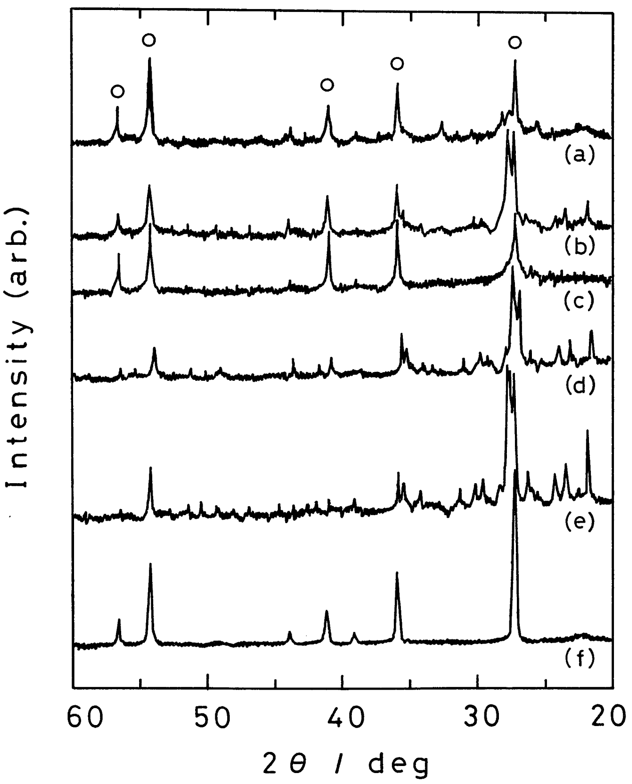

Fig. 9. The X-ray diffraction patterns of $xCaO \cdot (95-x)TiO_2 \cdot 5Fe_2O_3$ ceramics; (a): $x=10$, (b): $x=20$, (c): $x=30$, (d): $x=40$, (e): $x=50$. (f): The X-ray diffraction pattern due to TiO_2.

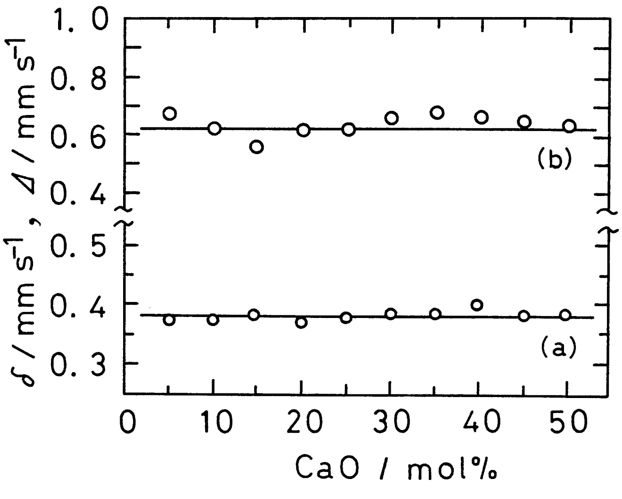

Fig. 10. The compositional dependence of (a): the isomer shift (δ) of the Fe^{3+} and (b): the quadrupole splitting (Δ) of the Fe^{3+} for the $xCaO \cdot (95-x)TiO_2 \cdot 5Fe_2O_3$ ceramics.

The isomer shift (δ) of the Fe^{3+} falls in the range of 0.37—0.40 mm s^{-1}, irrespective of the CaO content, and the average is 0.38 mm s^{-1} (Fig. 10a). The δ indicates the tetrahedral Fe^{3+}–O bond in the glassy phase of the $xCaO \cdot (95-x)TiO_2 \cdot 5Fe_2O_3$ glass-ceramics, since the δ of tetrahedral Fe^{3+} is reported to be equal to or less than 0.4 mm s^{-1}.[5—10] Almost identical δ values have been obtained in the case of $V(Fe)O_4$ tetrahedra constituting several vanadate glasses.[8—10] The δ of the octahedral Fe^{3+} is reported to be more than 0.42 mm s^{-1}, as was observed in the case of phosphate glasses.[18] Recently, Menil reported that the δ of tetrahedral Fe^{3+} is less than 0.30 mm s^{-1} (with respect to metallic iron (α-Fe)) in the case of several crystalline compounds, and that the δ of octahedral Fe^{3+} is more than 0.30 mm s^{-1}.[19] It is noted that the δ (0.30 mm s^{-1}), criterion between the octahedral and tetrahedral Fe^{3+} in crystals, is smaller than the corresponding δ (0.40 mm s^{-1}) reported for glasses.[5—10,18] The difference of the δ (0.40—0.30=0.10 mm s^{-1}) is ascribed to the difference of the mean Fe^{3+}–O bond length; the longer Fe^{3+}–O bond length will cause the larger δ values for the glasses. (It is well known that the molar volume of "glass" is larger than that of "crystal." This is also the case for each the bond length.) The δ of Fe^{3+} obtained for the $xCaO \cdot (95-x)TiO_2 \cdot 5Fe_2O_3$ ceramics (Fig. 10a) is much larger than that of the $xK_2O \cdot (95-x)TiO_2 \cdot 5Fe_2O_3$ glasses

(δ=0.20—0.23 mm s^{-1}) illustrated in Fig. 2, indicating the highly ionic character of the Fe^{3+}–O bond. The constant δ (Fig. 10a) suggests that a change of the CaO content results in little structural change in the Ti(Fe)O$_4$ tetrahedra. This is consistent with the compositional dependence of the Δ of Fe^{3+} obtained for the xCaO·(95−x)TiO$_2$·5Fe$_2$O$_3$ ceramics (Fig. 10b); the Δ is almost constant irrespective of the CaO content, having an average value of 0.63 mm s^{-1}. This means that the symmetry of TiO$_4$ and FeO$_4$ tetrahedra is little changed when the chemical composition is changed. The DTA curve of the xCaO·(95−x)TiO$_2$·5Fe$_2$O$_3$ ceramics comprises a broad exothermic curve, of which maximum is observed at the identical temperature of 384±1 °C. No endothermic peak corresponding to the T_g is observed in the DTA curve. The experimental results shown in Fig. 10 are quite different from those obtained for the xK$_2$O·(95−x)TiO$_2$·5Fe$_2$O$_3$ glasses (Figs. 2 and 4), in which the increase of K$_2$O content resulted in the decrease both of the δ and Δ owing to the formation of NBO in the Ti(Fe)O$_4$ tetrahedra.

The distinct change brought about in the xCaO·(95−x)TiO$_2$·5Fe$_2$O$_3$ ceramics is reflected in the relative absorption area of Fe^{3+} and Fe^{2+}, as is shown in Fig. 11. The relative absorption area (A) of the Fe^{3+} (fraction of the Fe^{3+}) decreases linearly from 94 to 75%, while that of the Fe^{2+} increases from 6 to 25% when the CaO content is stepwise increased from 5 to 50 mol%. A similar phenomenon was observed in the case of potassium phosphate glasses,[18] in which the electron transfer from the neighboring oxygen atom to the Fe^{3+} was speculated on the basis of the ESR measurements of the PO$_4^{2-}$ radicals produced by the γ-ray irradiation. Figures 10 and 11 suggest that the introduction of CaO into the TiO$_2$ matrix results in the reduction of Fe^{3+} into Fe^{2+}, without changing the δ and Δ of the Fe^{3+}.

The δ of Fe^{2+} falls in the range of 0.70—0.83 mm s^{-1}, having the average of 0.76 mm s^{-1}. These δ values indicate the presence of four-fold coordinated Fe^{2+} species.[15,19] (It is known that the δ of octahedral Fe^{2+} species is larger than 1.0 mm s^{-1}).[15,19] The δ values are almost constant irrespective of the CaO content, similarly to the case of the δ obtained for Fe^{3+} (Fig. 10a). The small δ for the Fe^{2+} (ca. 0.76 mm s^{-1}) indicates a strong covalency, reflecting a much shorter Fe^{2+}–O bond length. (It is considered that the short bond length was favorable for the electron transfer from oxygen to Fe^{3+}.) The Δ of Fe^{2+} falls in the range of 2.13—2.60 mm s^{-1}, being increased with an increasing CaO content. It is considered that the mixed valence state of Fe^{2+} and Fe^{3+} causes the decrease of the symmetry of Fe^{2+} O$_4$ tetrahedra.

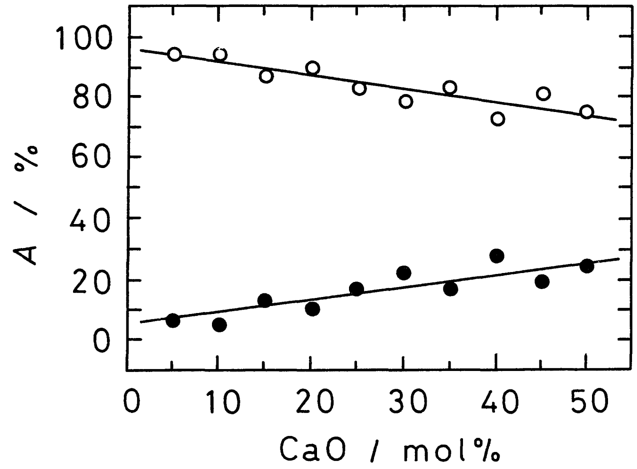

Fig. 11. Relative absorption area (fraction) of the Fe^{3+} (○) and that of the Fe^{2+} (●) obtained from the Mössbauer spectra of the xCaO·(95−x)TiO$_2$·5Fe$_2$O$_3$ ceramics.

Conclusion

1) In the K$_2$O–TiO$_2$–Fe$_2$O$_3$ glasses, the Fe^{3+} is substituted for the tetrahedral Ti^{4+}. This is confirmed from the Mössbauer and IR measurements. The Fe^{3+} plays a role of NWF.

2) The TiO$_4$ tetrahedra/TiO$_6$ octahedra ratio becomes higher in the K$_2$O–TiO$_2$ glasses when the K$_2$O content is increased.

3) The fraction of NBO in the TiO$_4$ tetrahedra also increases when the K$_2$O content is increased.

4) The K$_2$O–TiO$_2$–Fe$_2$O$_3$ glasses have the IR transparency. The transmission edge and the absorption edge are 5.4 and 7 μm, respectively.

5) A TiO$_2$ phase is precipitated in the matrix of the CaO–TiO$_2$–Fe$_2$O$_3$ ceramics.

6) Reduction of the Fe^{3+} into Fe^{2+} is observed in the CaO–TiO$_2$–Fe$_2$O$_3$ ceramics. This becomes noticeable with the increasing CaO content.

The authors are grateful to Prof. Yasukuni Matsumoto (Kinki University in Kyushu) for the help in the X-ray diffraction measurements. On of the authors, Tetsuaki Nishida, is indebted to the Japan Securities Scholarship Foundation for the financial support.

References

1) T. Yoshimaru, Y. Ueda, K. Morinaga, and T. Yanagase, *Yogyo Kyokai Shi*, **92**, 481 (1984).

2) T. Hanada, T. Aikawa, and N. Soga, *J. Am. Ceram. Soc.*, **67**, 52 (1984).

3) K. Kamiya, T. Yoko, and S. Sakka, *J. Mater. Sci.*, **20**, 906 (1985).

4) R. B. Greegor and F. W. Lytle, *J. Non-Cryst. Solids*, **55**, 27 (1983).

5) T. Nishida, H. Ide, and Y. Takashima, *Bull. Chem. Soc. Jpn.*, **63**, 548 (1990).

6) T. Nishida, H. Ide, T. Shinmyozu, Y. Takashima, and Y. Matsumoto, *Jpn. J. Appl. Phys.*, **29**, 1293 (1990).

7) T. Nishida, S. Saruwatari, and Y. Takashima, *Bull.*

Chem. Soc. Jpn., **61**, 2347 (1988).

8) T. Nishida, M. Ogata, and Y. Takashima, Proc. VI Int. Conf. Phys. Non-Cryst. Solids, Kyoto, 1987; *J. Non-Cryst. Solids*, **95/96**, 241 (1987).

9) T. Nishida, S. Saruwatari, and Y. Takashima, *Bull. Chem. Soc. Jpn.*, **61**, 2343 (1988).

10) T. Nishida, H. Ide, Y. Takashima, T. Yagi, S. Tomariguchi, T. Ishizuka, and A. Sakai, *J. Mater. Sci.*, **24**, 1687 (1989).

11) T. Nishida, S. Saruwatari, and Y. Takashima, *Bull. Chem. Soc. Jpn.*, **61**, 4093 (1988).

12) T. Nishida, M. Yamada, H. Ide, and Y. Takashima, *J. Mater. Sci.*, **25**, 3546 (1990).

13) P. Tarte, *Spectrochim. Acta*, **18**, 467 (1962).

14) L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, New York (1960), Chap. 13.

15) N. N. Greenwood and T. C. Gibb, "Mössbauer Spectroscopy," Chapman and Hall, London (1971), Chaps. 3 and 5.

16) T. Kokubo, M. Nishimura, and M. Tashiro, *J. Non-Cryst. Solids*, **22**, 125 (1976).

17) H. C. Hafner, N. J. Kreidl, and R. A. Weidel, *J. Am. Ceram. Soc.*, **41**, 315 (1958).

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

19) F. Menil, *J. Phys. Chem. Solids*, **46**, 763 (1985).