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Structural Relaxation of Semiconducting Vanadate and IR-Transmitting Gallate Glasses Containing Iron

Tetsuaki Nishida*

Department of Chemistry, Faculty of Science, Kyushu University
Hakozaki, Higashiku, Fukuoka 812-8581, Japan

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Glass transition temperature (T_g) is proportional to the quadrupole splitting (Δ) of Fe(III) obtained from the ^{57}Fe Mössbauer spectra ('T_g–Δ rules' (1990)). The values of Δ reflect the distortion of Fe(III) atoms, which occupy the sites of network-forming atoms. Heat treatment of potassium vanadate and calcium gallate glasses at around the individual T_g causes a structural relaxation, accompanying a linear decrease of T_g and Δ values. These experimental results prove that T_g decreases with a decrease in the distortion of VO_4, GaO_4, and FeO_4 tetrahedra, as the 'T_g–Δ rule' predicted.

Key words: Structural relaxation, Vanadate glass, Gallate glass, 'T_g–Δ rule', Distortion of network

I. Introduction

The Fe(III) occupies substitutional sites of network former (NWF) in several oxide glasses.[1-7] The quadrupole splitting (Δ) of Fe(III) observed in the Mössbauer spectra reflects the distortion of NWF sites, since Fe(III) has a symmetric electron configuration of $3d^5$ in the outer-most orbital and hence only the electric field gradient caused by the neighboring atoms is responsible for the magnitude of Δ value. Nishida *et al.* discovered that the glass transition temperature (T_g) of several inorganic glasses has a linear relationship with the Δ value of Fe(III).[1-7] This linear relationship, termed 'T_g–Δ rule', indicates that T_g is in proportion to the distortion of NWF. The 'T_g–Δ rule' is expressed by

$$T_g = a\Delta + b. \tag{1}$$

Slope of the straight line (a) in the plot of T_g vs. Δ becomes about 680°C (mm s^{-1})$^{-1}$ when Fe(III) occupies tetrahedral NWF sites, *i.e.*, Si(IV) and Ga(III) sites in silicate and gallate glasses, respectively.[1,2] Slope of the straight line (a) in the plot of T_g *vs.* Δ becomes 260°C (mm s^{-1})$^{-1}$ when Fe(III) occupies octahedral NWF sites, as observed for octahedral W(VI) in tungstate glasses.[3] Since octahedra generally have longer and weaker chemical bonds than tetrahedra, structure of octahedra will be easily modified than that of tetrahedra. A larger structural change of octahedral NWF will accompany a large change in the Δ values, giving rise to a smaller slope: 260°C (mm s^{-1})$^{-1}$. In the case of network modifier (NWM) like Na^+ and K^+, which has a coordination number (CN) ≥ 6, much larger structural change will bring about much smaller slope, *i.e.*, 35°C (mm s^{-1})$^{-1}$, as observed in phosphate, fluoride, and sulfate glasses.[1] The 'T_g–Δ rule' indicates that the site-occupation of Fe(III), whether NWF or NWM, and the distortion at the Fe(III) sites can be determined from the differential thermal analysis (DTA) and Mössbauer measurements.

Heat treatment of oxide glass will cause a decrease in the distortion of the structural units. As a result, a decrease of the Δ value of Fe(III) will be observed in the Mössbauer spectra. According to the 'T_g–Δ rule', a decrease of Δ value should accompany a decrease in the T_g. Structural relaxation of potassium silicate glass, $20K_2O \cdot 79SiO_2 \cdot {}^{57}Fe_2O_3$, was recently investigated by means of DTA and ^{57}Fe Mössbauer effect.[2] A linear decrease of T_g was observed in $20K_2O \cdot 79SiO_2 \cdot {}^{57}Fe_2O_3$ glass from 409°C to 386, 375, 346, and 316 (±5) °C after heat treatment at 450°C for 300, 600, 900, and 1500 min, respectively. At the same time, the Δ value of Fe(III) decreased linearly from 0.84 mm s^{-1} to 0.82, 0.81, 0.79, and 0.78 (±0.01) mm s^{-1}. These results suggest that the T_g of silicate glass is lowered when the distortion of SiO_4 and FeO_4 tetrahedra is reduced.

Lowering of T_g is equivalent to a decrease in the activation energy required for the cooperative movement of the fragments in the supercooled liquid, which exists in the temperature region between the T_g and the melting point (T_m).[2]

Semiconducting vanadate glass is composed of V_2O_5 and alkali-metal oxide or alkaline-earth metal oxide. V_2O_5 crystal has a layer structure composed of VO_5 pyramids.[8] An increase in the fraction of alkali-metal oxide or alkaline-earth metal oxide in the vanadate glass results in a step-by-step change of the network from the layer structure to a pseudo-one dimensional structure, as revealed by means of NMR,[9] IR,[10] and Mössbauer spectroscopy.[4-7,11,12] The NMR study performed by Segel and Creel[9] revealed that $50K_2O \cdot 50V_2O_5$ glass had a pseudo-chain structure composed of distorted VO_4 tetrahedra, similarly to the structure of KVO_3

crystal having a K_2O/V_2O_5 molar ratio of unity. These structural studies indicate that the fraction of VO_4 tetrahedra increases with an increasing content of alkali-metal oxide.

Electrical conductivity (σ) of $25K_2O \cdot 65V_2O_5 \cdot 10Fe_2O_3$ glass is of the order of 10^{-8} S cm^{-1} at room temperature.[12] The σ value increases to the order of 10^{-4} S cm^{-1}, owing to the structural relaxation, after heat treatment for 10 ~ 30 min at around the crystallization temperature (T_c). Mott *et al.*[13,14] proposed a *small polaron hopping theory* for the conduction mechanism of vanadate glass that is known to be a semiconductor caused by the electron hopping from V(IV) to V(V).

Gallate glasses are composed of distorted GaO_4 tetrahedra and small amounts of distorted GaO_6 octahedra.[15-19] They show a high optical transparency in the VIS-to-IR region. The IR-transmittance shows a significant decrease by heat treatment and by irradiations with laser or gamma-rays, as a result of crystallization.[16-19] Iron-containing gallate or aluminate glasses will be favorable for the study of crystallization or structural relaxation. In the crystallization study of $40CaO \cdot 59Ga_2O_3 \cdot Fe_2O_3$ glass by means of the DTA method (Kissinger plot), activation energy (E_a) of 5.5±0.2 eV was obtained by Kubuki *et al.*[17] Since the E_a value of iron-containing gallate glass was smaller than that of iron-free glass, it was concluded that the crystallization proceeded easily when parts of Ga(III) atoms were replaced by Fe(III).[17] This is also the case for aluminate glasses, in which a small amount of Al(III) atoms was replaced by Fe(III).[20]

The present study was carried out in order to verify the 'T_g–Δ rule' in structurally-relaxed semiconducting vanadate and IR-transmitting gallate glasses by means of DTA and Mössbauer spectroscopy. Fourier transform infrared (FTIR) spectra were measured in order to confirm the structural relaxation.

II. Experimental Procedure

A reagent mixture composed of K_2CO_3, V_2O_5, and Fe_2O_3 of guaranteed reagent grade was pulverized thoroughly in an agate mortar and melted at 1050°C for 1 h in an electric muffle furnace. Potassium vanadate glass containing iron, $25K_2O \cdot 65V_2O_5 \cdot 10Fe_2O_3$, of black color was prepared by quenching the melt with ice-cold water (only the outside the crucible was quickly immersed into water). A reagent mixture composed of $CaCO_3$, Ga_2O_3, and Fe_2O_3 of guaranteed reagent grade was melted at 1550°C for 2 h in an electric muffle furnace. Calcium gallate glass containing iron, $40CaO \cdot 55Ga_2O_3 \cdot 5Fe_2O_3$, was prepared by quenching the melt with ice-cold water. Heat treatment of the vanadate and gallate glasses was conducted in air using the electric muffle furnace. The value of T_g was determined by the conventional DTA conducted at a heating rate of 10°C min^{-1}. α-Al_2O_3 powder was used for the temperature calibration. ^{57}Fe Mössbauer spectra were measured at room temperature with a $^{57}Co(Pd)$ source of 3.7×10^8 Bq (10 mCi). A sheet of metallic-iron foil (α-Fe) enriched with ^{57}Fe was used as the reference for the isomer shift (δ) and for calibrating the velocity scale (*i.e.*, abscissa of the spectra). The spectra were analyzed by a least-squares method. FTIR spectra were recorded by the conventional KBr disk method.

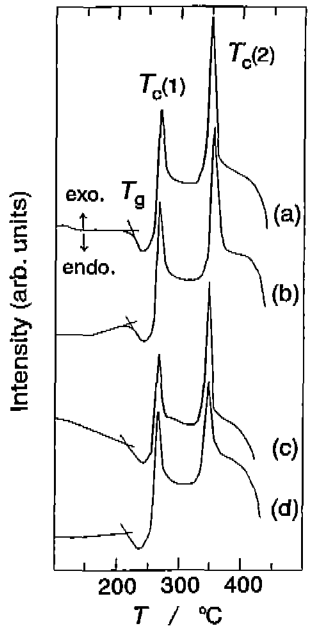

Fig. 1. DTA curves of $25K_2O \cdot 65V_2O_5 \cdot 10Fe_2O_3$ glass heat treated at 200°C for (a) 0, (b) 5, (c) 10 and (d) 120 min.

III. Results and Discussion

1. Vanadate glass

DTA curves of $25K_2O \cdot 65V_2O_5 \cdot 10Fe_2O_3$ glass heat treated at 200°C for ~120 min are illustrated in Fig. 1. The T_g value of the original glass was estimated to be 220 (±2) °C, as seen from Fig. 1(a). Two exothermic peaks (crystallization peaks) appearing at 269 (±2) and 350 (±2) °C in Fig. 1(a) are associated with the formation of KV_3O_8 phase.[12] The K_2O/V_2O_5 molar ratio in the KV_3O_8 crystal, *i.e.*, 1/3, is equal to the $K_2O/(V_2O_5+Fe_2O_3)$ ratio in $25K_2O \cdot 65V_2O_5 \cdot 10Fe_2O_3$ glass. We can understand from Fig. 1 that there occurred no remarkable structural change, such as crystallization and phase transition, and the heat-treated samples had essentially the same network (skeleton) structure as each other. Heat treatment of $25K_2O \cdot 65V_2O_5 \cdot 10Fe_2O_3$ glass at 200°C for 1, 2, 5, 10, and 15 min resulted in a step-by-step lowering of T_g from 220 to 210°C, reflecting the structural relaxation, and then it remained constant after the heat treatment for 20 ~ 120 min. These T_g values are plotted in Fig. 2 with open circles. The $T_c(1)$ value of this glass lowered gradually from 269 to 260 (±2) °C after heat treatment at 200°C for ~60 min and then it became constant after additional heat treatment. Similarly, the $T_c(2)$ value lowered gradually from 350 to 340 (±2) °C after heat treatment at 200°C for ~20 min and then became constant.

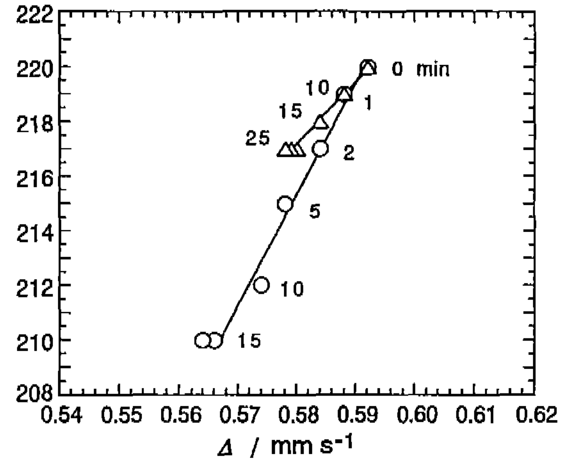

Fig. 2. Plots of the T_g against the Δ of Fe(III) obtained for $25K_2O \cdot 65V_2O_5 \cdot 10Fe_2O_3$ glass after heat treatment at 200 °C (○) and 170 °C (△).

Heat treatment of $25K_2O \cdot 65V_2O_5 \cdot 10Fe_2O_3$ glass at 170 °C for 10, 15, and 25 min resulted in a slight decrease of the T_g value from 220 to 217 (±2) °C, and became constant after additional heat treatment for ~180 min. These T_g values are plotted in Fig. 2 with open triangles. The $T_c(1)$ value decreased slightly from 269 to 266 (±2) °C after heat treatment at 170 °C for 35 min, while the $T_c(2)$ value remained constant at 350 °C. All the experimental results prove that the structural relaxation proceeds effectively at 200 °C than at 170 °C.

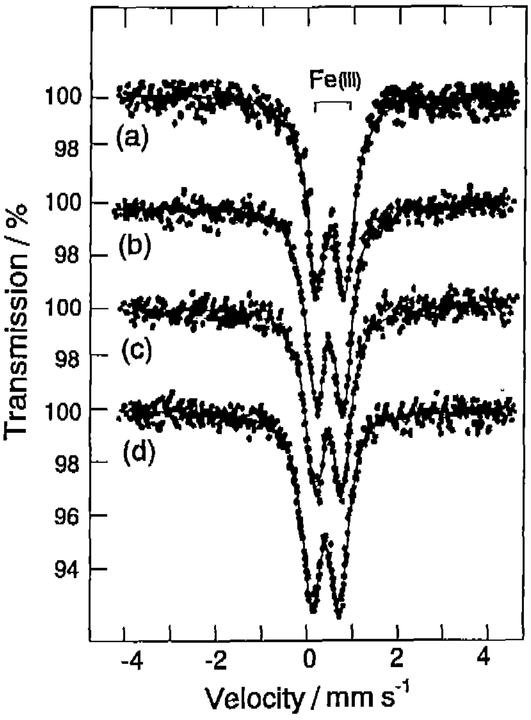

Fig. 3. Mössbauer spectra of $25K_2O \cdot 65V_2O_5 \cdot 10Fe_2O_3$ glass heat treated at 200 °C for (a) 0, (b) 5, (c) 10 and (d) 120 min.

Lowering of T_g should be observed with a decrease of Δ value, as described above. Some ^{57}Fe Mössbauer spectra of $25K_2O \cdot 65V_2O_5 \cdot 10Fe_2O_3$ glass heat treated at 200 °C for ~120 min are illustrated in Fig. 3. Each spectrum shows a quadrupole doublet due to tetrahedral Fe(III) with constant δ values of $0.39_2 \pm 0.004$ mm s⁻¹. Values of linewidth (Γ), $0.45_6 \pm 0.004$ mm s⁻¹, reflect "amorphous" structure at the Fe(III) sites. These Δ values are plotted in Fig. 2 with circles together with the T_g values described above. The Δ value decreased gradually from 0.59_2 mm s⁻¹ to 0.56_6 (±0.004) mm s⁻¹ by heat treatment at 200 °C for ~15 min, reflecting the structural relaxation. The Δ value remained constant after heat treatment for 20, 30, and 60 min and was 0.56_4 mm s⁻¹ after 120 min-treatment. All the Mössbauer parameters indicate that the heat treatment brings about only the decrease in the distortion of FeO_4 and VO_4 sites.

Heat treatment of $25K_2O \cdot 65V_2O_5 \cdot 10Fe_2O_3$ glass at 170 °C for 10, 15, and 25 min caused a very slight decrease of Δ value from 0.59_2 mm s⁻¹ to 0.58_0 (±0.004) mm s⁻¹, as plotted in Fig. 2 with triangles. The values of δ and Γ were independent of the heat treatment. Fig. 2 shows that the T_g decreases linearly with the Δ value by the heat treatment for ~15 min (circles) and for ~25 min (triangles) at around the T_g, owing to the structural relaxation. It is noted that both the T_g and Δ values became saturated after additional heat treatment. The decrease of T_g and that of Δ value are significant when the vanadate glass was heat treated at higher temperature (200 °C>170 °C).

IR spectroscopy is also effective for the crystallization study of glass. The stretching band generally becomes sharp and new band(s) due to the crystalline phase is often

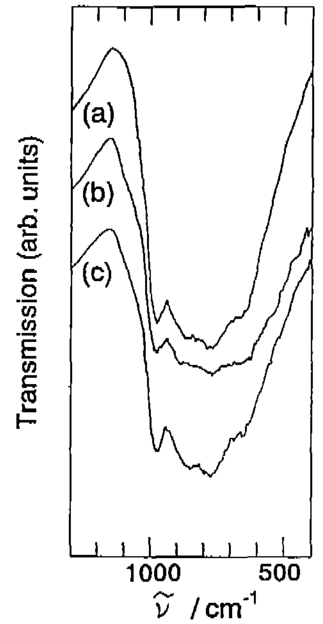

Fig. 4. FTIR spectrum of $25K_2O \cdot 65V_2O_5 \cdot 10Fe_2O_3$ glass; (a) original glass, (b) after heat treatment at 200 °C for 120 min and (c) after heat treatment at 170 °C for 180 min.

observed in glass-ceramics.[12,16-20] The FTIR spectra of $25K_2O \cdot 65V_2O_5 \cdot 10Fe_2O_3$ glass evidently show the structural relaxation, as illustrated in Fig. 4. The relative intensity of the stretching band due to V=O (1000 cm^{-1}) and V–O (850 cm^{-1}) in VO_5 pyramids were constant after heat treatment.

Relative intensity of V–O band (760 cm^{-1}) in VO_4 tetrahedra was also constant after heat treatment. Since the general feature of the FTIR spectra (Fig. 4) was not affected by the heat treatment, we can conclude that the heat treatment caused no prominent structural change in the network, such as the crystallization or the phase transition, and only the structural relaxation took place.

2. Gallate glass

DTA curve of $40CaO \cdot 55Ga_2O_3 \cdot 5Fe_2O_3$ glass is composed of one endothermic peak (T_g: 693±1°C) and two exothermic peaks ($T_c(1)$: 747±1°C, $T_c(2)$: 765±1°C), as shown in Fig. 5. Heat treatment of this glass at 670°C for 2, 5, and 10 min resulted in only the structural relaxation, and the T_g value lowered slightly from 693 to 690°C, as plotted in Fig. 6 (open circles). The $T_c(1)$ value remained almost constant at 747°C, while the $T_c(2)$ value lowered slightly from 765 to 762°C when the gallate glass was heat treated for ~ 10 min. After heat treatment at 670°C for more than 10 min, these peaks showed no change. These results mean that the structural relaxation becomes saturated or reaches equilibrium after 10-min treatment.

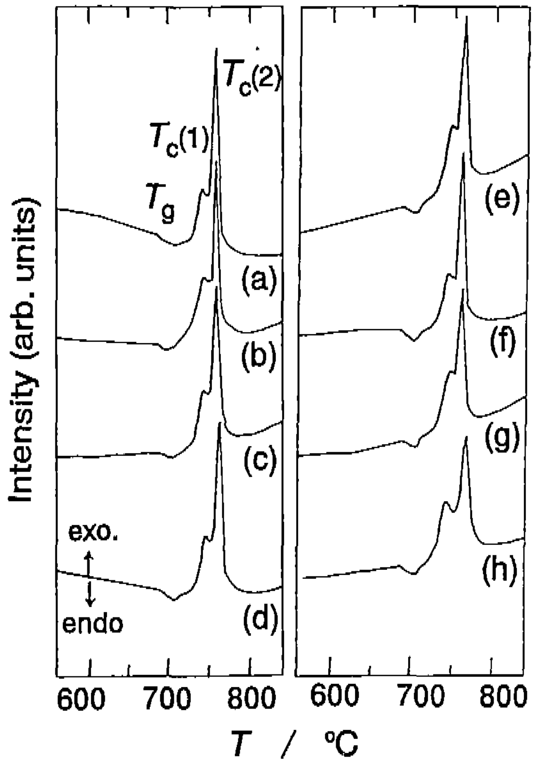

Fig. 5. DTA curves of $40CaO \cdot 55Ga_2O_3 \cdot 5Fe_2O_3$ heat treated at 670°C for (a) 0, (b) 2, (c) 5, (d) 10, (e) 20, (f) 40, (g) 60 and (h) 100 min.

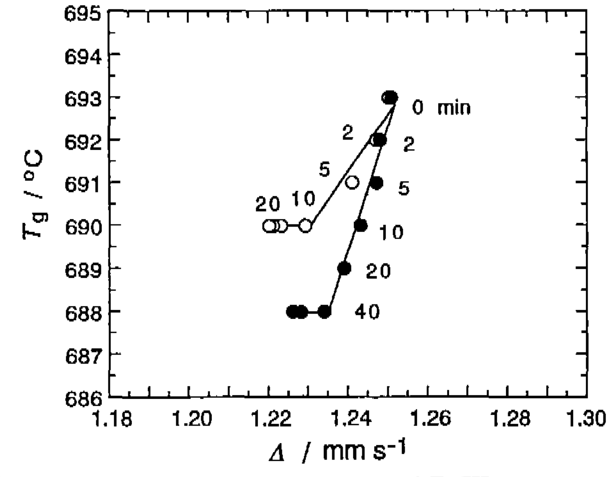

Fig. 6. Plots of the T_g against the Δ of Fe(III) obtained for $40CaO \cdot 55Ga_2O_3 \cdot 5Fe_2O_3$ after heat treatment at 670°C (○) and 690°C (●).

Heat treatment of $40CaO \cdot 55Ga_2O_3 \cdot 5Fe_2O_3$ glass at 690 °C for 2, 5, 10, 20, and 40 min caused a step-by-step lowering of T_g from 693 to 688°C, as plotted in Fig. 6 (solid circles). In these heat-treated samples, $T_c(1)$ and $T_c(2)$ values lowered gradually from 747 and 765°C to 744 and 760°C, respectively. After heat treatment at 690°C for 40 ~ 100 min, the exothermic peak of $T_c(2)$ became diminished owing to the partial crystallization and the formation of crystalline $CaGa_4O_7$ phase could be confirmed from the X-ray powder diffraction (XRD).

Mössbauer spectra of $40CaO \cdot 55Ga_2O_3 \cdot 5Fe_2O_3$ glass heat

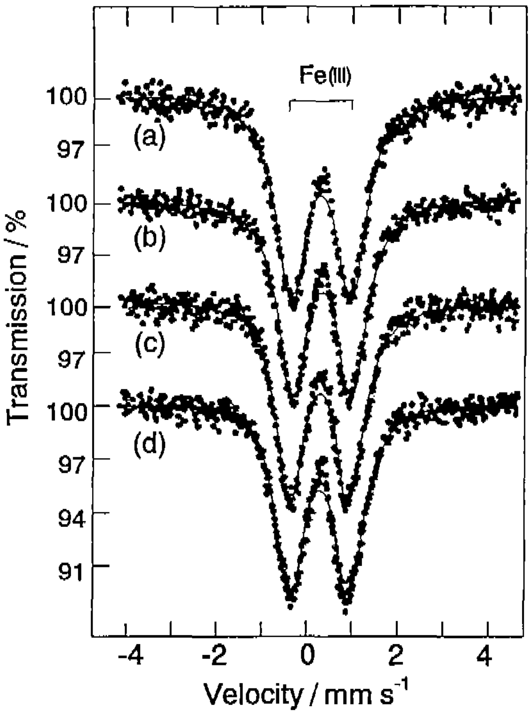

Fig. 7. Mössbauer spectra of $40CaO \cdot 55Ga_2O_3 \cdot 5Fe_2O_3$ after heat treatment at 670°C for (a) 0, (b) 10, (c) 20 and (d) 100 min.

treated at 670 °C are illustrated in Fig. 7. It can be understood from Figs. 7(a) and 3(a) that the quadrupole splitting of $40CaO \cdot 55Ga_2O_3 \cdot 5Fe_2O_3$ glass is much larger than that of $25K_2O \cdot 65V_2O_5 \cdot 10Fe_2O_3$ glass. The Mössbauer spectra showed a gradual decrease of the Δ value from 1.25_0 to 1.22_3 (± 0.004) mm s^{-1} after heat treatment at 670 °C for 2, 5, and 10 min, as plotted in Fig. 6 with open circles. The Δ value became nearly constant at 1.22_1 mm s^{-1} after heat treatment for 20 ~ 100 min.

The δ value decreased gradually from 0.28_9 to 0.26_5 (± 0.005) mm s^{-1} by heat treatment for ~20 min and then became constant. The small decrease of δ reflects a slightly increased covalency of the Fe(III)–O bonds in the FeO_4 tetrahedra. In these heat-treated samples, Γ value showed a decrease from 0.78_9 to 0.69_4 (± 0.004) mm s^{-1} and became nearly constant, reflecting an increased uniformity of Fe–O bond lengths and O–Fe–O angles.

Heat treatment of $40CaO \cdot 55Ga_2O_3 \cdot 5Fe_2O_3$ glass at 690 °C for ~100 min resulted in a step-by-step decrease of δ and Γ values. Asymmetric Mössbauer spectra were observed after heat treatment for 60 ~ 100 min. They were analyzed into two doublets: one doublet due to the crystalline phase with δ and Γ values of 0.26_5 and 0.56_9 mm s^{-1}, respectively, and the other due to the original glassy phase with δ and Γ values of 0.26_5 and 0.68_4 mm s^{-1}, respectively. The Δ value for the crystalline phase proved to be 1.07_6 mm s^{-1}.

Absorption area for the crystalline phase ($CaGa_4O_7$) increased with the duration of the heat treatment; *e.g.*, the absorption areas were 8.2 and 27.1% when the gallate glass was heat treated for 60 and 100 min, respectively. All the Δ values of Fe(III) obtained for the glassy phase of $40CaO \cdot 55Ga_2O_3 \cdot 5Fe_2O_3$ after heat treatment at 690 °C are plotted in Fig. 6 (solid circles). We can understand from Fig. 6 that the lowering of T_g is more pronounced at higher temperature (690 °C>670 °C), as observed in $25K_2O \cdot 65V_2O_5 \cdot 10Fe_2O_3$ glass (see Fig. 2). We can also understand from Figs. 2 and 6 that the structural relaxation of vanadate and gallate glasses at around the T_g does not proceed infinitely, but becomes saturated by the heat treatment for 25 and 40 min, respectively. Additional decrease of the Δ value in $40CaO \cdot 55Ga_2O_3 \cdot 5Fe_2O_3$ sample, observed after the T_g value was saturated (Fig. 6), is ascribed to partial crystallization. In these samples (glass-ceramics), structural information on the crystalline phase is available through the Fe(III) atoms, since they transfer from the original glassy phase to the crystalline phase.

The FTIR spectra of partially-crystallized $40CaO \cdot 55Ga_2O_3 \cdot 5Fe_2O_3$ glass is illustrated in Fig. 8(c). The stretching band due to GaO_4 tetrahedra[21] shows a peak shift from 666 (Fig. 8(a)) to 672 cm^{-1} (Fig. 8(c)). At the same time, the stretching band due to GaO_6 octahedra[21] shows a similar shift from 514 (Fig. 8(a)) to 530 cm^{-1} (Fig. 8(c)). The peak shift towards higher wavenumbers is ascribed to a slightly reduced Ga–O bond length in GaO_4 and GaO_6 units, as a result of partial crystallization. These FTIR results are consistent with the DTA, Mössbauer, and XRD results described above. The FTIR spectrum of $40CaO \cdot 55Ga_2O_3 \cdot 5Fe_2O_3$ sample heat treated at 690 °C for 40 min (Fig. 8(b)) has sharper absorption peaks than the original glass (Fig. 8(a)), indicating the onset of crystallization. The FTIR spectrum of $40CaO \cdot 55Ga_2O_3 \cdot 5Fe_2O_3$ sample heat treated at 670 °C for 10 min (Fig. 8(d)) is very similar to that of the original glass (Fig. 8(a)), reflecting that only the structural relaxation took place without crystallization.

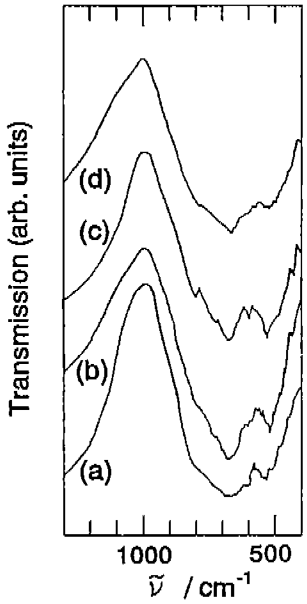

Fig. 8. FTIR spectrum of $40CaO \cdot 55Ga_2O_3 \cdot 5Fe_2O_3$ after heat treatment at 690 °C for (a) 0, (b) 40, c) 100 min and (d) at 670 °C for 10 min.

IV. Summary

1) Heat treatment of $25K_2O \cdot 65V_2O_5 \cdot 10Fe_2O_3$ and $40CaO \cdot 55Ga_2O_3 \cdot 5Fe_2O_3$ glasses at around the individual T_g results in the structural relaxation.

2) FTIR spectra of heat-treated $25K_2O \cdot 65V_2O_5 \cdot 10Fe_2O_3$ and $40CaO \cdot 55Ga_2O_3 \cdot 5Fe_2O_3$ glasses evidently show the structural relaxation.

3) DTA and Mössbauer measurements of the structurally-relaxed glasses show that T_g lowers linearly with a decrease of the Δ value of Fe(III), since it occupies the sites of distorted VO_4 and GaO_4.

4) The linear lowering of T_g observed in the structurally-relaxed glasses is ascribed to a decrease in the distortion of the NWF sites, as the 'T_g–Δ rule' (1990) predicted.

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