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Coordination state of Nb^{5+} ions in silicate and gallate glasses as studied by Raman spectroscopy

KOHEI FUKUMI, SUMIO SAKKA
Institute for Chemical Research, Kyoto University, Uji, Kyoto-Fu 611 and
Division of Molecular Engineering, Graduate School of Engineering, Kyoto University,
Sakyo-Ku, Kyoto 606, Japan

Raman spectra of K_2O–Nb_2O_5–SiO_2 glasses are measured in order to compare the coordination state of Nb^{5+} ions in gallate glasses with that in silicate glasses. It is found that less-distorted NbO_6 octahedra with no non-bridging oxygens as well as NbO_6 octahedra with non-bridging oxygens and/or with much distortion are present in the K_2O–Nb_2O_5–SiO_2 glasses. The Raman band in the 800 to 900 cm^{-1} region is attributed to the NbO_6 octahedra with non-bridging oxygens and/or with much distortion. The broad bands in the 600 to 800 cm^{-1} region are attributed to less-distorted NbO_6 octahedra with no non-bridging oxygens. An increase in the molar ratio Nb_2O_5/K_2O leads to an increase in the oxygens shared by more than two polyhedra and/or a decrease in non-bridging oxygens for the NbO_6 octahedra which possess non-bridging oxygens, or to an increase of distortion for much-distorted NbO_6 octahedra. At the same time, an increase in the molar ratio Nb_2O_5/K_2O increases the less-distorted NbO_6 octahedra with no non-bridging oxygens. In short, GaO_4 tetrahedra and NbO_6 octahedra compete to attract alkali ions in gallate glasses but such competition is not found in silicate glasses.

1. Introduction

Nb_2O_5 is known as an intermediate oxide for glass formation. It has been shown that in alkali niobium gallate glasses Ga^{3+} ions mainly form GaO_4 tetrahedra and Nb^{5+} ions distorted NbO_6 octahedra with a short Nb–O bond [1]. It is possible that there are complex interactions between NbO_6 octahedra and GaO_4 tetrahedra in alkali niobium gallate glasses, since a GaO_4 tetrahedron requires an alkali ion to compensate its excess negative charge and GaO_6 octahedra or oxygens shared by three GaO_4 tetrahedra are formed in gallate crystals when the alkali content is small. It is expected that the interaction between silicate and niobate anions in niobium-containing silicate glasses would be simpler than that between gallate and niobate anions in the niobium-containing gallate glasses, because the coordination number of silicon atoms for oxygens is usually constant at four in silicate glasses and a silicon atom does not require an alkali ion to form an SiO_4 tetrahedron. This indicates that a comparison of the structure of alkali niobium gallate glasses with that of alkali niobium silicate glasses will help us to understand the structural state of Nb^{5+} ions in gallate glasses.

K_2O–Nb_2O_5–SiO_2 glasses were selected for the study, considering that the K_2O–Nb_2O_5–SiO_2 system has a very wide glass-forming region in which the molar ratio Nb_2O_5/SiO_2 can be widely varied [2].

2. Experimental procedure

The compositions of the glasses prepared are shown in Fig. 1, in which the glass-forming region reported by Imaoka and Yamazaki [2] is also shown. Extra-pure K_2CO_3, Nb_2O_5 and SiO_2 were used as raw materials. The mixture of raw materials was melted at 1550° C for 30 min in a platinum crucible in an electrically heated furnace. The melt was poured on to an iron plate and pressed by another iron plate to form a glass plate 1 to 3 mm thick, which was used for the Raman scattering measurements. The Raman scattering measurement was made with a Japan Spectroscopic Co. (Jasco) Type NR-1000s laser-Raman spectrometer using the 514.5 nm line of an Ar^+ laser as the exciting beam.

3. Results

Raman spectra of $50K_2O \cdot 50SiO_2$ and $xK_2O \cdot (100 - 2x)Nb_2O_5 \cdot xSiO_2$ glasses are shown in Fig. 2. In the $50K_2O \cdot 50SiO_2$ glass, there are bands at 290 to 350 cm^{-1} and at about 575, 600, 835, 975 and 1025 cm^{-1}. The band at about 975 cm^{-1} is the strongest band in the 800 to 1100 cm^{-1} region. In the Raman spectra of $xK_2O \cdot (100 - 2x)Nb_2O_5 \cdot xSiO_2$ glasses, the largest band is located at 800 to 900 cm^{-1}. Other bands observed at about 600, 925 to 945 and about 1060 cm^{-1} have smaller intensities than the band at 800 to 900 cm^{-1}. The band at 800 to 900 cm^{-1} increases in intensity and the bands at about 600, 925 to 945 and about 1060 cm^{-1} decrease in intensity with increasing Nb_2O_5 content. The bands at about 600 and 1060 cm^{-1} are no longer found in the spectra of the glasses with 20 and 30 mol % Nb_2O_5, respectively. A broad band is

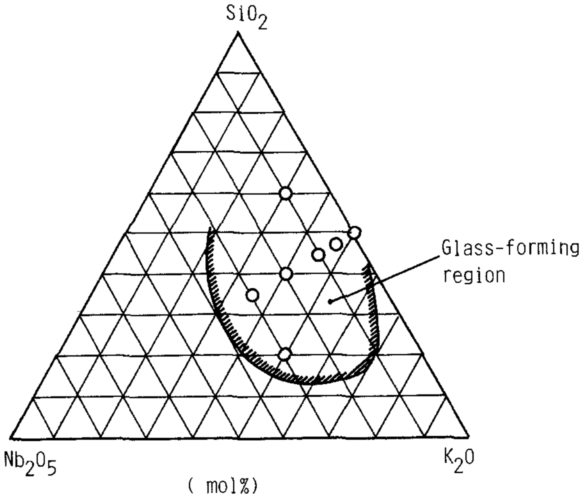

Figure 1 The compositions of glasses prepared in this work. The glass-forming region after Imaoka and Yamazaki [2] is also shown.

observed in the region 600 to 800 cm^{-1} in the spectra of the glasses with 20 and 30 mol % Nb_2O_5 and increases in intensity with increasing Nb_2O_5 content. The band at 800 to 900 cm^{-1} shifts toward higher wavenumbers with increasing Nb_2O_5 content. A band at about 230 cm^{-1} appears on the addition of Nb_2O_5 to $50K_2O \cdot 50SiO_2$ glass and increases in intensity with increasing Nb_2O_5 content. At the same time, the band at 290 to 350 cm^{-1} which is observed in the $50K_2O \cdot 50SiO_2$ glass decreases.

Raman spectra of the $50K_2O \cdot 30Nb_2O_5 \cdot 20SiO_2$ and $30K_2O \cdot 10Nb_2O_5 \cdot 60SiO_2$ glasses are shown in Fig. 3. A distinct band is observed at about 860 cm^{-1} in these glasses. The broad band in the 600 to 800 cm^{-1} region in these glasses is very weak. Small bands are found at about 540 and 1040 cm^{-1} in $50K_2O \cdot 30Nb_2O_5 \cdot 20SiO_2$ glass and at about 525 and 1090 cm^{-1} in $30K_2O \cdot 10Nb_2O_5 \cdot 60SiO_2$ glass. Two distinct bands are also observed at about 220 and 295 cm^{-1} in the former glass, and a broad band is observed at about 260 cm^{-1} in the latter glass.

4. Discussion

4.1. Band assignment

In silicate glasses, the bands near 850 cm^{-1}, near 900 cm^{-1}, at 950 to 1000 cm^{-1} and at 1050 to 1100 cm^{-1} have been assigned [3] to symmetric silicon–oxygen stretching motion of silicate units containing SiO_4 tetrahedra with four, three, two and one non-bridging oxygens, respectively, and the bands in the 400 to 700 cm^{-1} region are associated with the presence of bridging oxygens.

In the Nb_2O_5-containing silicate glasses, the band in the 800 to 900 cm^{-1} region is very strong compared with the bands at 600, 925 and 1055 cm^{-1}. The Raman spectra of alkali niobium gallate glasses show that a strong band due to NbO_6 octahedra is observed in the 800 to 900 cm^{-1} region [1]. Therefore, the band in the 800 to 900 cm^{-1} region in Nb_2O_5-containing silicate glasses can be attributed to NbO_6 octahedra.

The Raman peak wavenumbers of strong bands in niobate crystals hitherto reported are shown in Fig. 4. Crystals of MNb_2O_6 (M = Mg, Ca, Mn, Ni, Zn and Cd) [4], Li_3NbO_4 [5], $Mg_4Nb_2O_9$ [5], $Sr_3MgNb_2O_9$ [6]

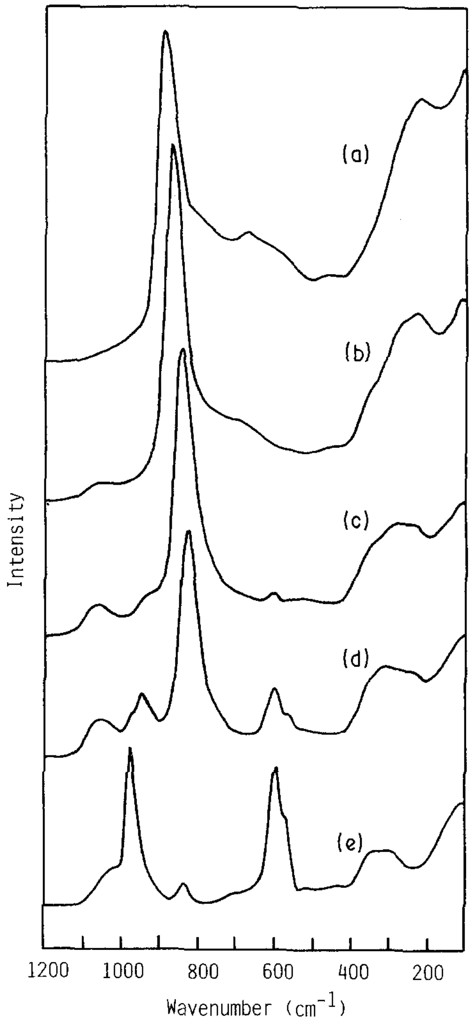

Figure 2 Raman spectra of $xK_2O \cdot (100 - 2x)Nb_2O_5 \cdot xSiO_2$ glasses: (a) $35K_2O \cdot 30Nb_2O_5 \cdot 35SiO_2$, (b) $40K_2O \cdot 20Nb_2O_5 \cdot 40SiO_2$, (c) $45K_2O \cdot 10Nb_2O_5 \cdot 45SiO_2$, (d) $47.5K_2O \cdot 5Nb_2O_5 \cdot 47.5SiO_2$, (e) $50K_2O \cdot 50SiO_2$.

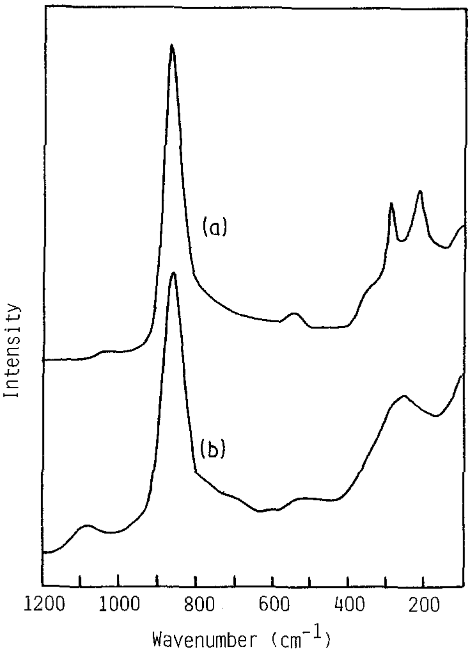

Figure 3 Raman spectra of (a) $50K_2O \cdot 30Nb_2O_5 \cdot 20SiO_2$ and (b) $30K_2O \cdot 10Nb_2O_5 \cdot 60SiO_2$ glasses.

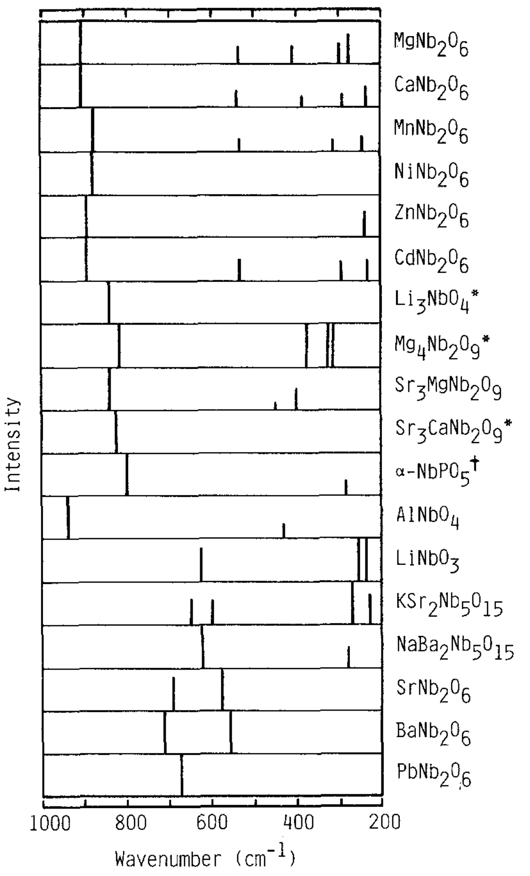

Figure 4 Strong bands observed in the Raman spectra of various niobate crystals. *Intensities are shown only by abbreviations, instead of schematic representation in reference. †Only the strong bands due to NbO_6 octahedra are shown.

and $Sr_3CaNb_2O_9$ [6] consisting of NbO_6 octahedra with non-bridging oxygens and α-$NbPO_5$ [7] and $AlNbO_4$ [8] consisting of much-distorted NbO_6 octahedra show a strong band at wavenumbers above $800\,cm^{-1}$. On the other hand, no distinct bands are found in this wavenumber region of the spectra of $LiNbO_3$ [9, 10], $BaNb_2O_6$ [11], $SrNb_2O_6$ [12], $PbNb_2O_6$ [13], $NaBa_2Nb_5O_{15}$ [10, 14] and $KSr_2Nb_2O_{15}$ [14] crystals which have no non-bridging oxygens. This indicates that the band due to NbO_6 octahedra in the 800 to $900\,cm^{-1}$ region of the Raman spectra of glasses can be assigned to the NbO_6 octahedra with non-bridging oxygens and/or with much distortion.

A strong band is found at 880 to $905\,cm^{-1}$ in the Raman spectra of MNb_2O_6 crystals [4] which consists of NbO_6 octahedra having a non-bridging oxygen, two oxygens shared by two NbO_6 octahedra and three oxygens shared by three NbO_6 octahedra [15]. On the other hand, a band is observed at about $840\,cm^{-1}$ in the Raman spectra of Li_3NbO_4 which consists of NbO_6 octahedra having three non-bridging oxygens and three oxygens shared by three NbO_6 octahedra [16]. This indicates that an increasing number of non-bridging oxygens in an NbO_6 octahedron which possesses non-bridging oxygens decreases the wavenumber of the band in the region above about $800\,cm^{-1}$. This band is observed at 810 to $840\,cm^{-1}$ in $Mg_4Nb_2O_9$ [5], $Sr_3MgNb_2O_9$ [6] and $Sr_3CaNb_2O_9$ [6] crystals, which consist of NbO_6 octahedra having three non-bridging oxygens and three oxygens shared by two NbO_6 octahedra [6, 17, 18], indicating that the peak wavenumber of the band in the region above $800\,cm^{-1}$ may decrease with a decreasing number of oxygens shared by three NbO_6 octahedra in an NbO_6 octahedron with non-bridging oxygens.

α-$NbPO_5$ consists of a chain of much-distorted NbO_6 octahedra having four oxygens shared with PO_4 tetrahedra and two oxygens shared with NbO_6 octahedra, and there are both short and long Nb–O bonds in an NbO_6 octahedron within the chain [19]. An $AlNbO_4$ crystal consists of much-distorted NbO_6 and AlO_6 octahedra. An NbO_6 octahedron has one oxygen shared by two octahedra, four oxygens shared by three octahedra and an oxygen shared by two octahedra and has two short Nb–O bonds and two long Nb–O bonds [20]. The band due to NbO_6 octahedra is observed at about 800 and $940\,cm^{-1}$ in the spectra of the former and the latter crystals, respectively [7, 8]. This indicates that an increase of distortion and/or increase in the number of the oxygens shared by three or four polyhedra may increase the peak wavenumber of the band in the region above about $800\,cm^{-1}$.

The broad band found in the 600 to $800\,cm^{-1}$ region increases in intensity with increasing Nb_2O_5 content of $xK_2O \cdot (100 - 2x)Nb_2O_5 \cdot xSiO_2$ glasses, indicating that this band is concerned with Nb^{5+} ions. As the bands in the 500 to $800\,cm^{-1}$ region are found in niobate crystals which have no non-bridging oxygens, such as $LiNbO_3$ [9, 10], $BaNb_2O_6$ [11], $SrNb_2O_6$ [12], $PbNb_2O_6$ [13], $NaBa_2Nb_5O_{15}$ [10, 14] and $KSr_2Nb_5O_{15}$ [14], the broad bands found in the 600 to $800\,cm^{-1}$ region in these glasses are attributed to the less-distorted NbO_6 octahedra with no non-bridging oxygens.

4.2. Structure of K_2O–Nb_2O_5–SiO_2 glasses

In the Raman spectrum of $50K_2O \cdot 50SiO_2$, bands are observed at about 575, 600, 835, 975 and $1025\,cm^{-1}$. The band at about $975\,cm^{-1}$ is the strongest band in the 800 to $1100\,cm^{-1}$ region, indicating that SiO_4 tetrahedra with two non-bridging oxygens are the main structural unit in the glass.

In the Raman spectra of K_2O–Nb_2O_5–SiO_2 glasses, the bands due to silicate units decrease in intensity with increasing Nb_2O_5 content, indicating that the concentration of silicate units decreases and that of niobate units increases with increasing Nb_2O_5 content. The band due to silicate units is already very weak compared with the band in the 800 to $900\,cm^{-1}$ region in $47.5K_2O \cdot 5Nb_2O_5 \cdot 47.5SiO_2$ glass. This has not been caused by a decrease of silicate units but by the strong intensity of the band at about 800 to $900\,cm^{-1}$ due to NbO_6 octahedra.

In the Raman spectra of $xK_2O \cdot (100 - 2x)Nb_2O_5 \cdot xSiO_2$ glasses, the broad band in the 600 to $800\,cm^{-1}$ region increases with increasing Nb_2O_5 content. On the other hand, in $50K_2O \cdot 30Nb_2O_5 \cdot 20SiO_2$ glasses, the broad band in the 600 to $800\,cm^{-1}$ region is small. This indicates that the less-distorted NbO_6 octahedra with no non-bridging oxygens increase with increasing molar ratio Nb_2O_5/K_2O.

In K_2O–Nb_2O_5–SiO_2 glasses, the band in the 800 to $900\,cm^{-1}$ region is the major band due to NbO_6 octahedra and the broad band in the 600 to $800\,cm^{-1}$

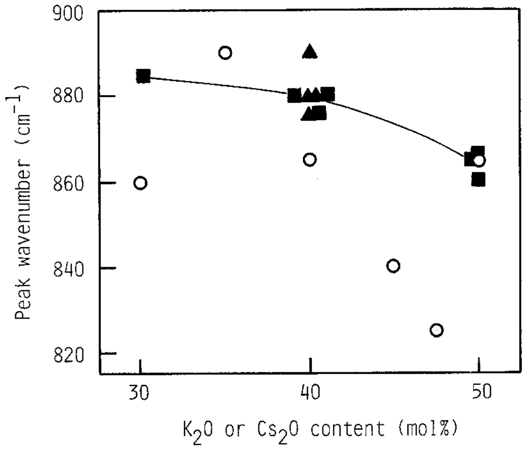

Figure 5 Peak wavenumbers of the band in the 800 to 900 cm^{-1} region in the Raman spectra of different glasses [1] against K_2O or Cs_2O content: (○) K_2O–Nb_2O_5–SiO_2, (▲) K_2O–Nb_2O_5–Ga_2O_3, (■) Cs_2O–Nb_2O_5–Ga_2O_3.

region increases with increasing molar ratio Nb_2O_5/K_2O. This indicates that Nb^{5+} ions form mainly the NbO_6 octahedra with non-bridging oxygens and/or with much distortion when the molar ratio Nb_2O_5/K_2O is small, and that the less-distorted NbO_6 octahedra with no non-bridging oxygens increase and the NbO_6 octahedra with non-bridging oxygens and/or much distortion decrease with increasing molar ratio Nb_2O_5/K_2O.

The peak wavenumber of the band at 800 to 900 cm^{-1} is plotted against K_2O content and the molar ratio Nb_2O_5/K_2O in Figs 5 and 6, respectively, where the peak wavenumbers of the band in alkali niobium gallate glasses are also shown [1]. As shown in Figs 5 and 6, the peak wavenumber of the band in the 800 to 900 cm^{-1} region depends on the molar ratio Nb_2O_5/K_2O rather than the K_2O content in the silicate glasses, indicating that an increase of Nb_2O_5 content relative to K_2O content leads to a decrease of non-bridging oxygens in an NbO_6 octahedron, an increase in the oxygens shared by more than two polyhedra, and/or an increase in the distortion of NbO_6 octahedra.

The band in the 950 to 1000 cm^{-1} region is observed at about 975 cm^{-1} in $50K_2O \cdot 50SiO_2$ glass, and the band shifts toward lower wavenumbers with increasing Nb_2O_5 content. In the potassium silicate glasses, the band at about 975 cm^{-1} shifts to 935 cm^{-1} with decreasing K_2O content [21]. This suggests that the content of network-modifying oxide decreases with increasing Nb_2O_5 content; that is, Nb_2O_5 does not act as a network modifier.

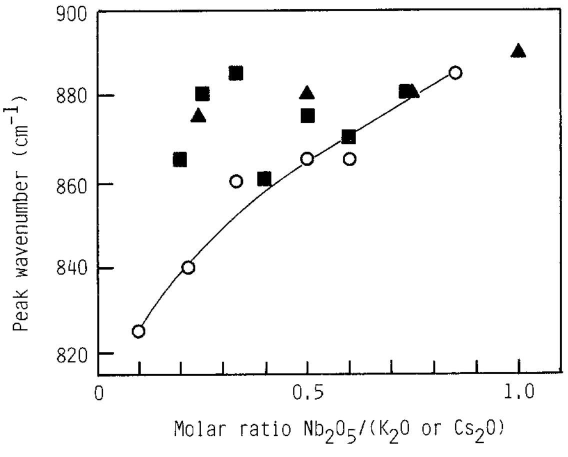

Figure 6 Peak wavenumbers of the band in the 800 to 900 cm^{-1} region in the Raman spectra of different glasses [1] against the ratio of Nb_2O_5 content to the K_2O or Cs_2O content: (○) K_2O–Nb_2O_5–SiO_2, (▲) K_2O–Nb_2O_5–Ga_2O_3, (■) Cs_2O–Nb_2O_5–Ga_2O_3.

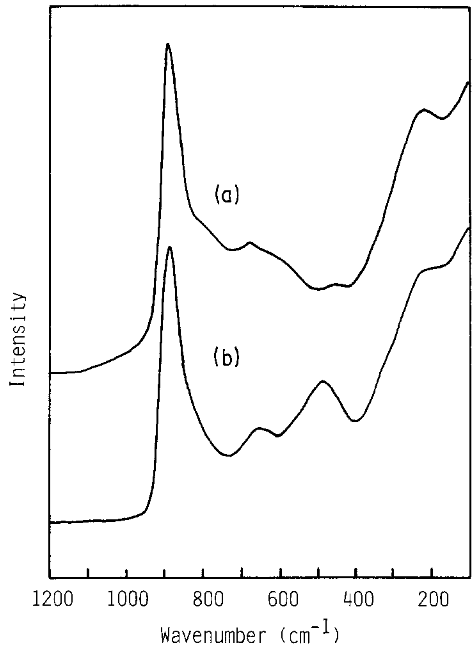

Figure 7 Comparison of Raman spectrum of (a) $35K_2O$–$30Nb_2O_5$–$35SiO_2$ glass with that of (b) $40K_2O$–$30Nb_2O_5$–$30Ga_2O_3$ glass [1].

4.3. Comparison of the Raman spectra of silicate glasses with gallate glasses

Raman bands due to NbO_6 octahedra observed in alkali niobium gallate glasses [1] are also observed in alkali niobium silicate glasses as shown in Fig. 7, indicating that the coordination state of Nb^{5+} ions observed in gallate glasses is similar to that in silicate glasses. However, the dependences of the peak wavenumber of the band in the 800 to 900 cm^{-1} region on glass composition are different. The peak wavenumber in the silicate glasses depends on the ratio of alkali oxide to Nb_2O_5 oxide rather than the alkali oxide content, as shown in Figs 5 and 6. In other words, it does not depend on the SiO_2 content. On the other hand, in the gallate glasses, the peak wavenumber mainly depends on the alkali oxide content [1], as shown in Fig. 5; that is, the peak wavenumber mainly depends on both Ga_2O_3 content and Nb_2O_5 content. As Ga^{3+} ions require alkali ions to compensate the excess negative charge of GaO_4 tetrahedra in the gallate glasses, GaO_4 tetrahedra and NbO_6 octahedra compete to take alkali ions. On the other hand, such a requirement is not necessary for SiO_4 tetrahedra in silicate glasses, and NbO_6 octahedra in silicate glasses can obtain alkali ions more freely than in the gallate glasses. Therefore, the peak wavenumber of the band in the 800 to 900 cm^{-1} region depends on the molar ratio of Nb_2O_5/K_2O and the alkali oxide content, respectively, in the silicate glasses and gallate glasses.

5. Conclusion

It has been shown that the broad band in the 600 to

800 cm^{-1} region is attributed to the less-distorted NbO_6 octahedra with no non-bridging oxygens in silicate glasses. In the silicate glasses, Nb^{5+} ions form less-distorted NbO_6 octahedra with no non-bridging oxygens as well as NbO_6 octahedra with non-bridging oxygens and/or much distortion. The peak wavenumber of the band in the 800 to 900 cm^{-1} region increases and the band in the 600 to 800 cm^{-1} increases in intensity with increasing molar ratio Nb_2O_5/K_2O, indicating that an increase of the molar ratio Nb_2O_5/K_2O leads to a decrease in the non-bridging oxygens and/or an increase in the oxygens shared by more than two polyhedra in NbO_6 octahedra which possess non-bridging oxygens, or it leads to an increase in the distortion of the much-distorted NbO_6 octahedra. At the same time, an increase of the molar ratio Nb_2O_5/K_2O leads to an increase in the less-distorted NbO_6 octahedra with no non-bridging oxygens. In summary, it has been shown that GaO_4 tetrahedra and NbO_6 octahedra compete to take alkali ions in gallate glasses, but in silicate glasses such a competition is not necessary for NbO_6 octahedra.

Acknowledgement

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References

1. K. FUKUMI and S. SAKKA, *J. Non-Cryst. Solids* **84** (1986) 100.
2. M. IMAOKA and T. YAMAZAKI, *Rep. Inst. Industr. Sci., Univ. Tokyo*, **18**(4) (1968) 1.
3. P. McMILLAN, *Amer. Mineral.* **69** (1984) 622.
4. E. HUSSON, Y. REPELIN, NGUYEN QUY DAO and H. BRUSSET, *Spectrochim. Acta* **33A** (1977) 995.
5. G. BLASSE and G. P. M. VAN DEN HEUVEL, *Z. Phys. Chem. N.F.* **84** (1973) 114.
6. G. BLASSE and A. F. CORSMIT, *J. Solid State Chem.* **10** (1974) 39.
7. G. T. STRANFORD and R. A. CONDRATE, *ibid.* **52** (1984) 248.
8. G. BLASSE and R. U. E. 'tLAM, *ibid.* **25** (1978) 77.
9. R. F. SCHAUFELE and M. J. WEBER, *Phys. Rev.* **152** (1966) 705.
10. S. D. ROSS, *J. Phys. C* **3** (1970) 1785.
11. Y. REPELIN, E. HUSSON and H. BRUSSET, *Spectrochim. Acta* **35A** (1979) 937.
12. Y. REPELIN, E. HUSSON, NGUYEN QUY DAO and H. BRUSSET, *ibid.* **35A** (1979) 1165.
13. *Idem*, **36A** (1980) 253.
14. G. BURNS, J. D. AXE and D. F. O'KANE, *Solid State Commun.* **7** (1969) 933.
15. J. P. GUMMINGS and S. H. SIMONSEN, *Amer. Mineral.* **55** (1970) 90.
16. J.-C. GRENIER, C. MARTIN and A. DURIF, *Bull. Soc. Fr. Miner. Crist.* **87** (1964) 316.
17. E. F. BERTAUT, L. CORLISS, F. FORRAT, R. ALEONARD and R. PAUTHENET, *J. Phys. Chem. Solids* **21** (1964) 234.
18. F. GALASSO and J. PYLE, *Inorg. Chem.* **2** (1963) 482.
19. J. M. LONGO and P. KIERKAGAARD, *Acta Chem. Scand.* **20** (1966) 72.
20. B. F. PEDERSEN, *ibid.* **16** (1962) 421.
21. S. A. BRAWER and W. B. WHITE, *J. Chem. Phys.* **63** (1975) 2421.

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