JOURNAL OF MATERIALS SCIENCE **26** (1991) 248–252

Structure of $Na_2O \cdot 2TiO_2$ glass

F. MIYAJI, T. YOKO, H. KOZUKA, S. SAKKA
Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu 611, Japan

X-ray radial distribution analysis and Raman spectroscopic measurement were carried out on $Na_2O \cdot 2TiO_2$ glass prepared by twin-roller quenching method. It is found that four-coordinated Ti^{4+} ions may be predominant over six-coordinated ones in the present glass. It is also found that the fraction of six-coordinated Ti^{4+} ions is larger in the present glass than in $K_2O \cdot 2TiO_2$ and $Cs_2O \cdot 2TiO_2$ glasses. Poorer glass-forming ability of the Na_2O–TiO_2 system compared with the K_2O–TiO_2 and Cs_2O–TiO_2 systems is ascribed to a larger fraction of TiO_6 octahedron for the former system.

1. Introduction

TiO_2 is not classified into a glass-forming oxide, but an intermediate oxide which does not form glass by itself [1]. It is known, however, that TiO_2 forms glass on addition of a second component such as alkali and alkaline earth oxides [2–4]. In previous studies the authors investigated the structure of K_2O–TiO_2 and Cs_2O–TiO_2 binary glasses by means of X-ray radial distribution function analysis and Raman spectroscopy, concluding that most of Ti^{4+} ions in the glasses are coordinated by four oxygens, although a very small portion of Ti^{4+} ions in the six oxygen coordination coexist [6, 7].

The Na_2O–TiO_2 system is known to have less glass-forming ability than the K_2O–TiO_2 and Cs_2O–TiO_2 systems [4]. This is probably due to less basicity of Na_2O compared with K_2O and Cs_2O, since the glass-forming ability of TiO_2-based glasses increases with increasing basicity of the second additives [4]. In most oxide crystals, Ti^{4+} ions are six-coordinated by oxygen. Taking into account that glass formation in oxide glass is closely related to the coordination number of cations of the oxides which constitute networks, it is interesting to study the structure of Na_2O-containing titanate glass, especially the coordination number of Ti^{4+} ions, and compare with K_2O- and Cs_2O-containing glasses. In the present work X-ray radial distribution analysis on $Na_2O \cdot 2TiO_2$ glass is reported. The results are discussed with the help of measurements of Raman spectrum and the density, in order to estimate the coordination number of Ti^{4+} ions in the glass. The glass-forming ability of alkali titanate systems is also discussed.

2. Experimental procedures

2.1. Preparation of samples

The glass of the composition $Na_2O \cdot 2TiO_2$ was prepared by quenching the melt with a twin-roller. About 6 g of the well mixed glass batch consisting of extra pure reagents of Na_2CO_3 and TiO_2 was melted in a platinum crucible at 1350 °C for 30 min using an electric furnace. About 80% of the quenched melt was devitrified, and about 20% became clear glass. The clear pieces were collected and used as a sample. The sample was confirmed to be amorphous by X-ray diffraction.

The density of the glass was measured by a pycnometric method.

2.2. Measurement and analysis of X-ray scattering intensity

The X-ray scattering intensities were measured on fine glass powders prepared by pulverizing the thin glass sheet. A Rigaku-Denki model Geiger flex RAD II-A X-ray diffractometer was employed. MoKα ($\lambda = 0.0709$ nm) radiation was used. The intensity measurements were made in the range of $S\,(= 4\pi \sin\theta/\lambda)$ from 8.0 to 140.6 nm^{-1} by step scanning at intervals of 0.5° in 2θ. The input power was adjusted to 50 kV–35 mA. The measurement by 100 sec fixed time method was repeated until the accumulative intensities exceeded 10 000 counts at each point. The average accumulative intensity at each angle was taken as the scattered X-ray intensity.

The intensity curve was normalized after being corrected for polarization and Compton scattering. The experimental amplitude function $Si(S)$ was calculated from the normalized intensity. Then the $Si(S)$ was transformed into the radial distribution function RDF. Further details of the analysis was mentioned in the previous paper [6].

2.3. Measurement of Raman spectrum

The Raman spectrum was measured on the thin sheet of $Na_2O \cdot 2TiO_2$ glass with Nippon Bunko Model JASCO NR-1000S laser Raman spectrometer using the 514.5 nm line of an Ar^+ laser as the exciting beam. The power was adjusted to 250 mW.

3. Results

3.1. Glass formation in the $Na_2O \cdot 2TiO_2$ system

In the present Na_2O–TiO_2 system, the glass formation region by quenching with a twin-roller was limited to

0022–2461/91 $03.00 + .12

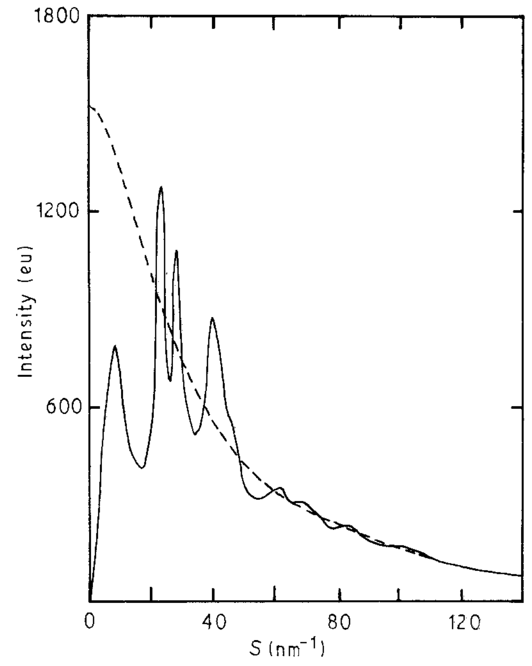

Figure 1 The X-ray scattering intensity curve for $Na_2O \cdot 2TiO_2$ glass. The broken line denotes the independent scattering per $Na_2O \cdot 2TiO_2$.

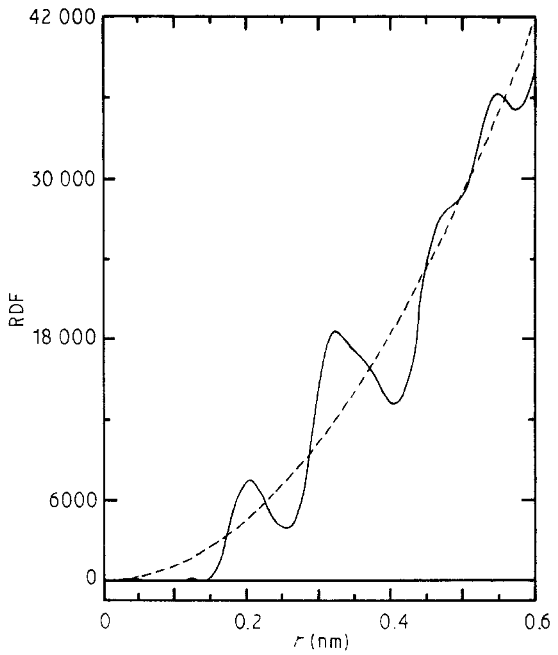

Figure 3 The radial distribution function curve for $Na_2O \cdot 2TiO_2$ glass. The broken line denotes the averaged electron density curve.

the composition 33.3 mol % Na_2O ($Na_2O \cdot 2TiO_2$ composition) and only about 20% of the melt became glass. It was very difficult for other compositions of the Na_2O–TiO_2 system to form glass. The glass formation region of the Na_2O–TiO_2 system is narrower by far than that of the K_2O–TiO_2 system, that is, the K_2O–TiO_2 system forms glass in the range of about 30 to 60 mol % K_2O by the same method, and in addition, more than 90% of the $K_2O \cdot 2TiO_2$ melt becomes clear glass [8].

3.2. RDF and DRDF curves

Figs 1 and 2 show the normalized X-ray intensity and the modified experimental amplitude function $Si(S)\exp(-\alpha^2S^2)$ curves, respectively. Fig. 3 shows the RDF curve obtained by the Fourier transformation of $Si(S)\exp(-\alpha^2S^2)$, where peaks are found at 0.203, 0.322 and 0.548 nm and shoulders at about 0.47 nm. The differential RDF curve, DRDF, is shown in Fig. 4. Clear peaks are found at 0.199, 0.318, 0.468 and 0.537 nm in the DRDF curve.

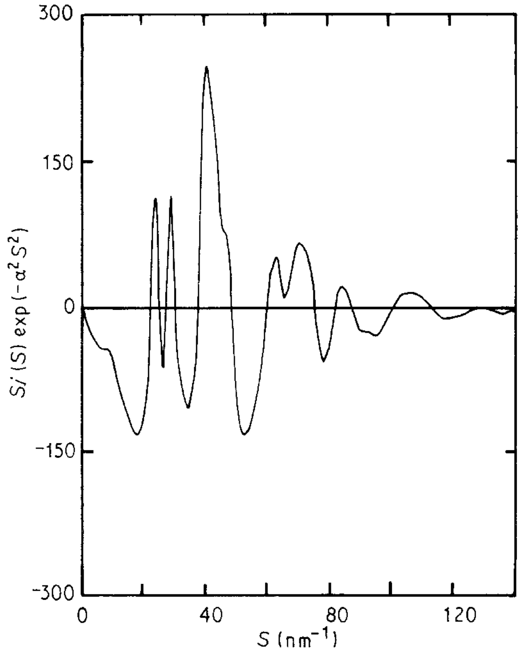

Figure 2 The experimental amplitude function curve $Si(S)$ for $Na_2O \cdot 2TiO_2$ glass.

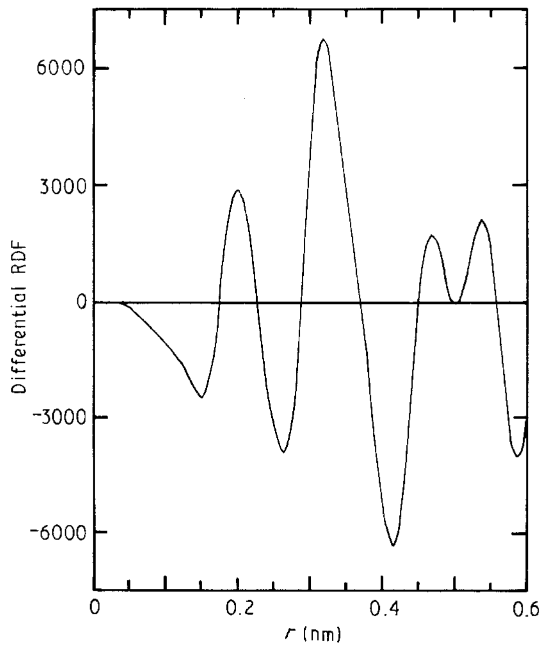

Figure 4 The differential radial distribution function curve for $Na_2O \cdot 2TiO_2$ glass.

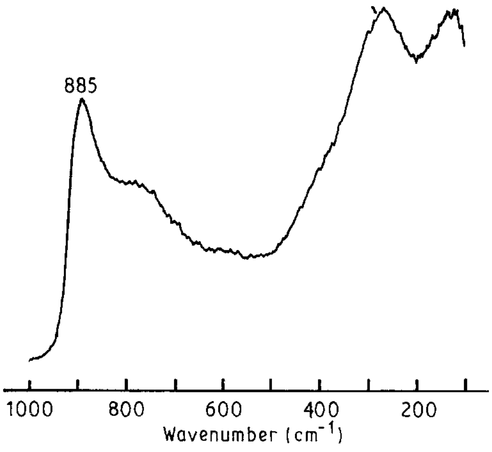

Figure 5 Raman spectrum of $Na_2O \cdot 2TiO_2$ glass.

3.3. Raman spectrum of $Na_2O \cdot 2TiO_2$ glass

Raman spectrum of $Na_2O \cdot 2TiO_2$ glass is shown in Fig. 5. A strong peak at 885 cm^{-1}, fairly strong peaks at 125 and 270 cm^{-1}, a weak band at about 600 cm^{-1} and a shoulder at 750 cm^{-1} are observed. The spectral profile of the present glass is similar to those of K_2O–TiO_2 and Cs_2O–TiO_2 glasses obtained in the previous study [7].

3.4. Density

The measured density of the glass was 3.02 gcm^{-3}, which is higher than 2.80 gcm^{-3}, density for the $K_2O \cdot 2TiO_2$ glass [2].

4. Discussion

4.1. Glass structure

The first peak at 0.199 nm in the RDF curve shown in Fig. 4 is mainly due to the Ti–O pair. The radial distribution function RDF_{cal} was calculated for this peak to examine the oxygen coordination number of Ti^{4+} ions. It has been reported that Ti^{4+} ions are four- or six-coordinated by oxygens in alkali titanate glasses [2–4]. Two types of coordination states are, therefore, considered in the present $Na_2O \cdot 2TiO_2$ glass.

Figs 6 and 7 compare the calculated and observed RDF curves expressed by solid and broken lines, respectively. It is seen from Fig. 6 that the calculated peak area is much larger than the observed one when all the Ti^{4+} ions are assumed to be six coordinated. On the other hand, Fig. 7 shows that the calculated peak area is slightly smaller than the observed one when all the Ti^{4+} ions are assumed to be four coordinated. This may indicate that both four- and six-coordinated Ti^{4+} ions are present in the $Na_2O \cdot 2TiO_2$ glass, although the former ions are predominant.

In Table I the first peak position due to Ti–O pair in the $Na_2O \cdot 2TiO_2$ glass is compared with that in the $K_2O \cdot 2TiO_2$ glass previously reported [6]. As clearly seen in the table, the former is longer than the latter by 0.011 nm. It is also found that the width of the first peak in the $Na_2O \cdot 2TiO_2$ glass is larger than that in the $K_2O \cdot 2TiO_2$ glass [6]. As the Ti–O interatomic distance in the TiO_6 unit should be by about more than 0.01 nm longer than in the TiO_4 unit [6], these

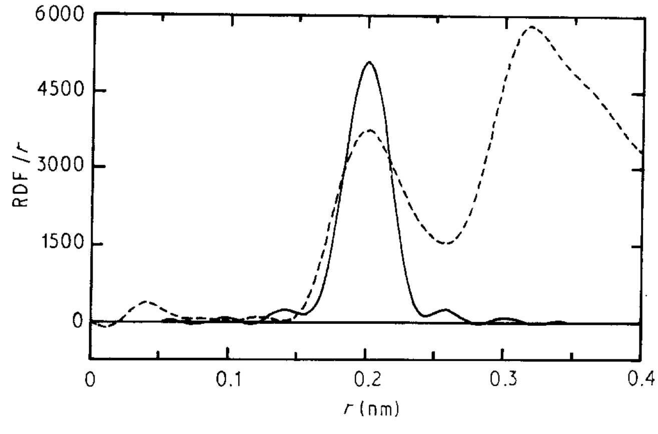

Figure 6 RDF/r and pair distribution function curves for six-coordinated Ti^{4+} ions with r(Ti–O) set to 0.200 nm. The solid and broken lines show the calculated and observed RDF/r curves, respectively.

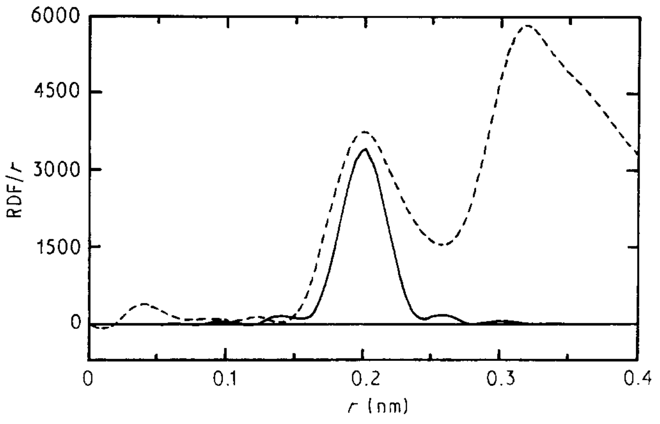

Figure 7 RDF/r and pair distribution function curves for four-coordinated Ti^{4+} ions with r(Ti–O) set to 0.200 nm. The solid and broken lines show the calculated and observed RDF/r curves, respectively.

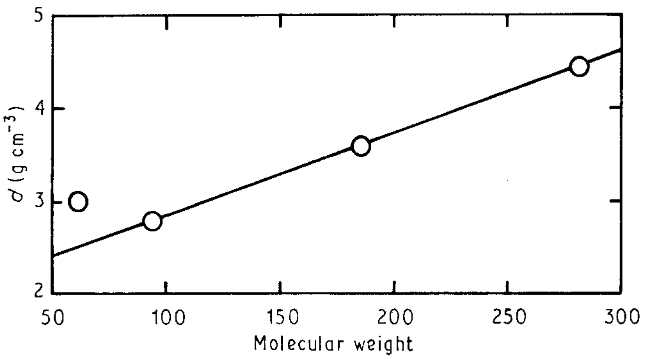

Figure 8 The relation between the densities of $R_2O \cdot 2TiO_2$ glasses *d* and the molecular weight of R_2O.

facts also indicate that a considerable amount of six-coordinated Ti^{4+} ions is present in addition to four-coordinated Ti^{4+} ions in the $Na_2O \cdot 2TiO_2$ glass.

There may be also the contribution of the Na–O pair to the first peak on the higher *r* side because the calculated Na–O distance is 0.237 nm if the coordination numbers of Na^+ and O^{2-} ions are assumed to be six and two, respectively [9, 10]. The calculation indicates that the Na–O pairs contribute considerably to the first peak on the higher *r* side. It is difficult, however, to determine the exact fraction of the six-coordinated Ti^{4+} ions, because the distribution of the Na–O distance and the average coordination number of Na^+ ions are not clear.

The comparison of the peak positions besides the first peak in the DRDF curves obtained for the $Na_2O \cdot 2TiO_2$ and $K_2O \cdot 2TiO_2$ [6] glasses is also made in Table I. The large second peak at 0.318 nm for the $Na_2O \cdot 2TiO_2$ glass reflects mostly the heavier pairs such as Ti–Ti and Na–Ti. Such heavier pairs in the $Na_2O \cdot 2TiO_2$ glass may be distributed at the lower *r* than in the $K_2O \cdot 2TiO_2$ glass which has the corresponding peak at 0.366 nm. A larger number of peaks are observed in the range of $r < 0.6$ nm in the $Na_2O \cdot 2TiO_2$ glass than in the $K_2O \cdot 2TiO_2$ glass. This indicates that the structural order of the former glass is retained up to a longer distance than in the latter.

A strong peak at 885 cm^{-1} in the Raman spectrum of $Na_2O \cdot 2TiO_2$ glass (Fig. 5) reflects the predominant TiO_4 tetrahedral units [7]. In the region from 500 to 850 cm^{-1}, there are many overlapping bands. Among them weak and broad bands can be seen at 600 and 750 cm^{-1}. The former band possibly corresponds to TiO_6 octahedral units [7]. This assignment can be deduced from the fact that this (600 cm^{-1}) band is not found in the Raman spectrum of $2Na_2O \cdot TiO_2$ glass in which all the Ti^{4+} ions are assumed to take four coordination [11].

TABLE I. The peak positions and their assignment in the RDF curves in the region of $r < 0.6$ nm for the $Na_2O \cdot 2TiO_2$ and $K_2O \cdot 2TiO_2$ glasses

$Na_2O \cdot 2TiO_2$		$K_2O \cdot 2TiO_2$ [6]	
Position (nm)	Pair	Position (nm)	Pair
0.199	Ti–O, Na–O	0.188	Ti–O
		0.297	K–O, O–O
0.318	Ti–Ti, Na–Ti	0.366	Ti–Ti, K–Ti
0.468	Na–Na, Ti–O		Ti–O
0.537			

The latter band at about 750 cm^{-1} is not to be assigned to such a band, although the peak at about 750 cm^{-1} observed in the $42.9Cs_2O \cdot 57.1TiO_2$ glass was assigned to the Ti–O_{nb} (where O_{nb} denotes non-bridging oxygen) stretching vibration in TiO_4 units with non-bridging oxygens [7]. There should be more non-bridging oxygens in $2Na_2O \cdot TiO_2$ glass than in $Na_2O \cdot 2TiO_2$ glass. Nevertheless, the shoulder at 750 cm^{-1} for the former is weaker than the latter, indicating that this band can not be related only to non-bridging oxygens. Mysen *et al.* suggested that the band at 720 cm^{-1} for $2Na_2O \cdot TiO_2$ glass reflects O–Ti–O deformation [11]. It is assumed that the 720 cm^{-1} -band observed for Na_2O–TiO_2 glasses increases in intensity with increasing TiO_6 octahedral units because the strain of O–Ti–O bonding or distortion of TiO_x polyhedra ($x = 4$ or 6) may increase as the fraction of TiO_6 octahedra increases. It is conceivable that such a band is weaker for $2Na_2O \cdot TiO_2$ glass than for $Na_2O \cdot 2TiO_2$ glass because the former is likely to have few TiO_6 units.

Fig. 8 shows the relation between the densities of $R_2O \cdot 2TiO_2$ (R=Na, K, Rb and Cs) glasses *d* and the molecular weight of R_2O. The density values for $R_2O \cdot 2TiO_2$ glasses other than $Na_2O \cdot 2TiO_2$ glass are taken from Rao's work [2]. A complete linear relationship is seen between *d* and the molecular weight of R_2O for $K_2O \cdot 2TiO_2$, $Rb_2O \cdot 2TiO_2$ and $Cs_2O \cdot 2TiO_2$ glasses, indicating that these glasses are structurally similar in the sense that most Ti^{4+} ions are four-coordinated. On the other hand, a large deviation from a linear relationship is found for the $Na_2O \cdot 2TiO_2$ glass, indicating that this glass is structurally different from other alkali dititanate glasses, that is, characterized by a higher fraction of six-coordinated Ti^{4+} ions.

Briefly, it can be said that most Ti^{4+} ions are four-coordinated, although a considerably larger fraction of Ti^{4+} ions are six coordinated in $Na_2O \cdot 2TiO_2$ glass compared with $K_2O \cdot 2TiO_2$, $Rb_2O \cdot 2TiO_2$ and $Cs_2O \cdot 2TiO_2$ glasses.

4.2. Glass-forming ability

The glass-forming ability of alkali titanate glasses will be discussed on the basis of the result that the fraction of the six-coordinated Ti^{4+} ions in the $Na_2O \cdot 2TiO_2$

glass is larger than in the $K_2O \cdot 2TiO_2$ glass. As mentioned in Section 3.1., the glass-forming range is quite limited in the Na_2O–TiO_2 system and the $Na_2O \cdot 2TiO_2$ is the unique composition which can form glass. Melts of other compositions solidify as crystals even with twin-roller quenching, also, only about 20% of the melt of the composition $Na_2O \cdot 2TiO_2$ forms glass. On the other hand, the melts containing K_2O form glass in the wide composition range of 30 to 60 mol % K_2O and most of the quenched melt of the composition $K_2O \cdot 2TiO_2$ becomes glass by twin-roller quenching [8]. Yoshimaru *et al.* determined the glass formation regions of the Na_2O–TiO_2 and K_2O–TiO_2 systems with the splat quenching method and reported that the respective glass formation region is 20 to 45 mol % Na_2O and 15 to 65 mol % K_2O [4]. Although it is widened by using the splat quenching method, the glass formation region in the Na_2O–TiO_2 system is considerably narrower than in the K_2O–TiO_2 system. A clear glass can easily be obtained only by pouring the melts onto an iron plate in the Cs_2O–TiO_2 system [5]. No glass can be obtained in the Li_2O–TiO_2 system [5, 8], that is, the glass-forming ability of alkali titanate systems increase in the order Li_2O–TiO_2 < Na_2O–TiO_2 < K_2O–TiO_2 < Cs_2O–TiO_2.

Zachariasen [1] indicated that the glass forming tendency is strong for oxides of cations with higher valencies and smaller coordination numbers, that is, three and four. The authors have shown that most Ga^{3+} and Al^{3+} ions are four-coordinated in Ga_2O_3- and Al_2O_3-based glasses although these cations are most likely to be six-coordinated in oxide crystals [12, 13]. This indicates that Zachariasen's theory applies not only to glass-forming cations such as Si^{4+}, B^{3+}, Ge^{4+}, P^{5+} and As^{3+} but to other cations.

The structure of glass can be closely related to that of high-temperature melt because glass is a frozen melt, thus it can be assumed that the fraction of the six-coordinated Ti^{4+} ions generally decreases in the order Li_2O–TiO_2 > Na_2O–TiO_2 > K_2O–TiO_2 > Cs_2O–TiO_2. The average coordination number of the high-valency cation of Ti^{4+} should increase in the order Cs_2O–TiO_2 < K_2O–TiO_2 < Na_2O–TiO_2 < Li_2O–TiO_2 because the theoretical basicity Λ_{th} [14] of the glass decreases in the order Cs_2O–TiO_2 > K_2O–TiO_2 > Na_2O–TiO_2 > Li_2O–TiO_2 when alkali oxides are additives, which agrees with the conclusion drawn above.

5. Conclusion

X-ray radial distribution analysis and Raman spectroscopic measurement were applied to $Na_2O \cdot 2TiO_2$ glass prepared by twin-roller quenching method. It has been found that a major portion of Ti^{4+} ions are four coordinated, although a considerable fraction of Ti^{4+} ions are six coordinated in the $Na_2O \cdot 2TiO_2$ glass compared with the $K_2O \cdot 2TiO_2$ and $Cs_2O \cdot 2TiO_2$ glasses. The poorer glass-forming ability of the Na_2O–TiO_2 system is due to the lower basicity compared with the K_2O–TiO_2 and Cs_2O–TiO_2 systems.

Acknowledgements

We would like to thank Mr K. Tanaka, Kyoto University for operating the twin-roller quenching apparatus to prepare the samples. This work was supported by the Grant-in-Aid for Scientific Research (No. 02403016) of Ministry of Education, Science and Culture, Japan.

References

1. W. H. ZACHARIASEN, *J. Amer. Chem. Soc.* **54** (1932) 3841.
2. BH. V. J. RAO, *J. Amer. Ceram. Soc.* **47** (1964) 455.
3. H. RAWSON, in "Inorganic Glass-Forming Systems" (Academic Press, London, 1967) p. 201.
4. K. YOSHIMARU, Y. UEDA, K. MORINAGA and T. YANAGASE, *Yogyo-Kyokai-Shi* **92** (1984) 481.
5. T. KOKUBO, Y. INAKA and S. SAKKA, *J. Non-Cryst. Solids* **95&96** (1987) 547.
6. S. SAKKA, F. MIYAJI and K. FUKUMI, *ibid.* **107** (1989) 171.
7. S. SAKKA, F. MIYAJI and K. FUKUMI, *ibid.* **112** (1989) 64.
8. Unpublished data
9. K. H. SUN, *J. Amer. Ceram. Soc.* **30** (1947) 277.
10. R. D. SHANNON, *Acta Crystallogr.* **A32** (1976) 751.
11. B. O. MYSEN, F. J. RYERSON and D. VIRGO, *Amer. Mineral.* **65** (1980) 1150.
12. K. FUKUMI and S. SAKKA, *J. Non-Cryst. Solids* **95&96** (1987) 193.
13. S. SAKKA, *Yogyo-Kyokai-Shi* **85** (1977) 168.
14. J. A. DUFFY and M. D. INGRAM, *J. Non-Cryst. Solids* **21** (1976) 373.

Received 31 July 1989
and accepted 19 February 1990