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X-ray Diffraction Study of Alkali Titanate Glasses

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A Fourier analysis of X-ray diffraction spectra of vitreous $2TiO_2.K_2O$ and $2TiO_2.Cs_2O$ is presented. The Ti^{4+} ion is shown to be *octahedrally* co-ordinated with respect to oxygen, the interionic Ti-O distance being equal to 1.95 Å. The K^+ and Cs^+ ions are not distributed at random but are placed in contact with the three oxygens of the faces of TiO_6 octahedra constituting the network. This proves conclusively that a glass network former is capable of a regular octahedral co-ordination and shows the further need to revise the classic Zachariasen-Warren theory.

1. Introduction

Alkali titanate glasses were first obtained by Baynton, Rawson, and Stanworth in 20 mg quantities [1]. Rao prepared glasses in the binary systems K_2O-TiO_2, Rb_2O-TiO_2 and Cs_2-TiO_2 in the composition range 34 to 67 mole % TiO_2 in 1 to 5 g batches and made an extensive study of their physical properties [2].

Infra-red spectra seemed to indicate that no change of co-ordination of the Ti^{4+} ion occurred when the percentage of alkali was increased and the building block in these glasses was assumed to be the TiO_6 octahedron, but no conclusive evidence was obtained. Rao's results were criticised by White [3] who attempted to explain infra-red spectra on the basis of a strong carbonate contamination. This criticism does not seem justified [4], carbonate ions being possibly only a minor contamination. Anyhow, in the absence of an X-ray structural analysis, the question of the co-ordination of Ti^{4+} ions in the alkali titanate glasses remained unresolved.

The present paper describes such a study for glasses of compositions $2TiO_2.K_2O$ and $2TiO_2.Cs_2O$.

2. Experimental Method

$2TiO_2.K_2O$ glass was prepared from pure TiO_2 and Na_2CO_3 (Prolabo R.P.). The batch was desiccated at 110° C for 1 h, then reacted in a platinum crucible at about 1000° C. The temperature was slowly raised to 1300° C and maintained at that level for 15 min. A few lamellae of clear glass of about 0.1 mm thickness were obtained by quenching the melt between two iron blocks refrigerated by water. The infrared spectrum of this glass was identical to that given by Rao [2]. The specimens were stored in sealed evacuated tubes until use.

$2TiO_2.Cs_2O$ glass was similarly prepared from TiO_2 (pure R.P. Prolabo) and Cs_2CO_3 (Merck) reacted in a platinum crucible at 1050° C. The temperature was increased to 1120° C and maintained at this level for 10 min. Glass was obtained by quench as before, and kept in evacuated tubes.

X-ray diffraction spectra were obtained by the photographic method, using an evacuated focussing camera of 125 mm diameter, associated with a curved quartz monochromator. Spectra were recorded using strictly monochromatic MoKα radiation ($\lambda = 0.70$ Å). Exposure times ranged from 90 to 150 h for 45 KV, 6 mA operating conditions. A few faint lines, indicating a slight devitrification, could be detected in the spectra of some specimens.

The intensity data obtained from microphotometric records were corrected for absorption in the sample, polarisation effect in the specimen and the monochromator and camera form factor.

3. Analysis of the Spectra

Measured intensity was fitted to the calculated sum of independent and Compton scattering using Norman's method [5]. Figs. 1 and 2 show respectively the diffraction spectra of $2TiO_2.K_2O$ and $2TiO_2.Cs_2O$ glasses normalised in this way. Intensity is expressed in electron units, the

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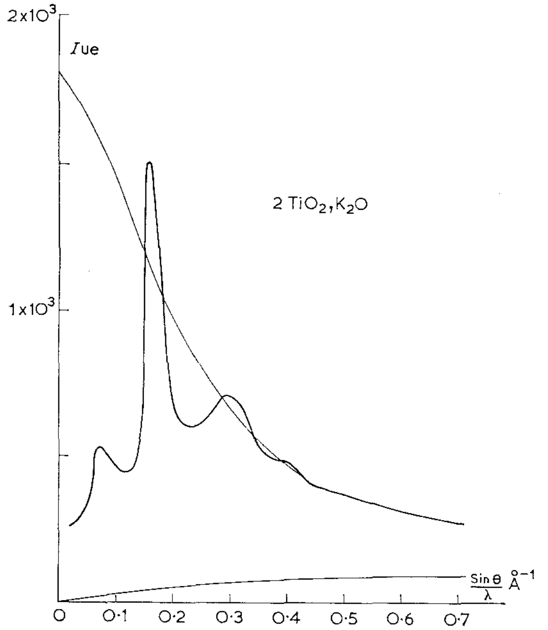

Figure 1 X-ray diffraction spectrum of vitreous $2TiO_2.K_2O$.

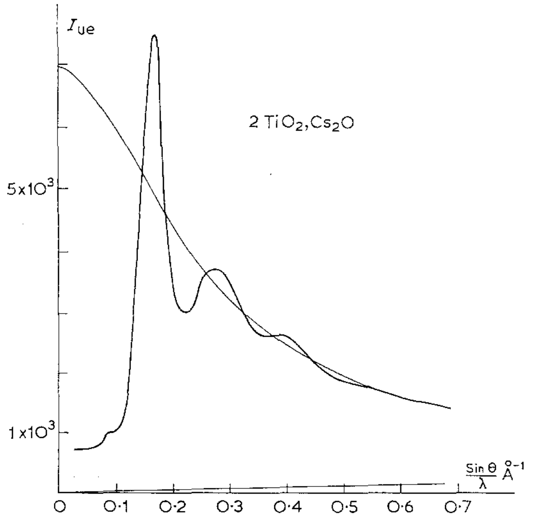

Figure 2 X-ray diffraction spectrum of vitreous $2TiO_2.Cs_2O$.

independent coherent and Compton scattering being evaluated for the stoichiometric composition units indicated. Ionic scattering factors were used throughout the calculations. Normalised spectra were Fourier-transformed in the classical way [6] to obtain the radial distribution functions.

A radial distribution function is defined by the expression

$$\sum_m K_m 4\pi r^2 \rho_m(r) = \sum_m K_m 4\pi r^2 \rho_0 + \frac{2r}{\pi}\int_0^\infty s.i(s) \sin rs \, ds \quad \ldots . (1)$$

where $s = 4\pi \sin\theta/\lambda$ (θ-scattering angle), r a radial distance; $\sum_m$ indicates the summation over a stoichiometric unit. K_m is the effective electronic number of the atom m, defined by $K_m = (f_m/f_e)$, where f_m is the scattering factor of the atom m, and f_e the average scattering factor of an electron, defined by $f_e = \sum_m f_m / \sum_m Z_m$, where Z_m is the atomic number of atom m. Since the effective electronic numbers K_m are functions of s in the actual integration range (O, s_0), average values $\bar{K}_m$ are used, defined by

$$\bar{K}_m = \frac{1}{s_0}\int_0^{s_0} K_m \, ds \qquad (2)$$

The average electron density ρ_0 is obtained from the expression

$$\rho_0 = Nd \sum_m Z_m / M \qquad (3)$$

where d is the density, M the molar mass and N Avogadro's number. The scattered intensity function $si(s)$ to be transformed is defined by the expression:

$$si(s) = s[I_{coh} - \sum_m f_m{}^2]/f_e{}^2 \qquad (4)$$

where the coherent intensity $I_{coh} = I_{measured} - I_{Compton}$, is expressed in electronic units after normalisation. The integral

$$\frac{2r}{\pi}\int_0^{s_0} s.i(s) \sin rs \, ds$$

was evaluated using a high speed electronic computer for r values from 0 to 10 Å at intervals of 0.1 Å.

The integration range was limited to $s_0 = 8$ Å^{-1} and no damping factor was applied to the intensity function. Table I presents the numerical data used in analysing the two glasses, i.e. the average effective electronic numbers $\bar{K}_m$ of the ions and the density of the glasses at 20° C, taken from Rao [2].

TABLE I

	$\bar{K}_{Ti^{4+}}$	$\bar{K}_{O^{2-}}$	$\bar{K}_{K^+}$	$\bar{K}_{Cs^+}$	$d_{20°C}$
$2TiO_2K_2O$	22.0	7.4	20.3	—	2.80
$2TiO_2Cs_2O$	19.5	6.7	—	60.6	4.49

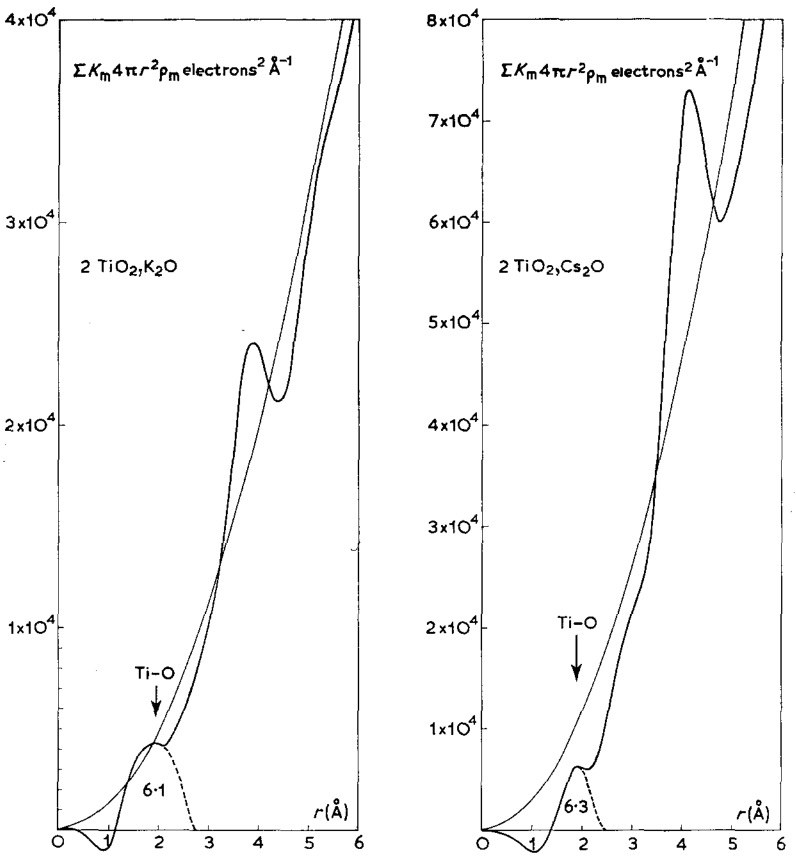

Figure 3 Radial distribution functions of vitreous $2TiO_2.K_2O$ (left) and $2TiO_2.Cs_2O$ (right).

4. Interpretation of Results

Fig. 3 shows the radial distribution function computed in this way for the ($2TiO_2.K_2O$) and ($2TiO_2.Cs_2O$) glasses. The two functions are very similar. Both have a slight but clearly perceptible maximum at 1.95 Å and a second pronounced peak situated at 3.90 Å for the potassium and at 4.15 Å for the caesium glass, respectively. This second peak is further discussed below. The first peak obviously corresponds to the Ti-O interatomic distance, which for crystalline TiO_2 varies between 1.91 and 2.01 Å according to the allotropic variety considered. For example in rutile, four Ti-O distances are equal to 1.92 and two to 2.01 Å, while in brookite the six Ti-O distances vary between 1.92 and 1.98 Å and in anatase four Ti-O are equal to 1.91 Å and two to 1.95 Å. In some compounds the distances are shorter; thus, in ilmenite, $FeTiO_3$, Ti-O = 1.89 Å and in perovskite, $CaTiO_3$, Ti-O = 1.88 Å.

In our study the area corresponding to the first peak of the radial distribution curve was delimited by symmetry from the leading edge. These areas A (Ti-O) indicated on fig. 3 correspond to 4500 and 3700 (electron units)² for the $2TiO_2.K_2O$ and $2TiO_2.Cs_2O$ respectively.

From an area A (Ti-O) the average co-ordination number n_0^{Ti} of titanium ion with respect to oxygen may be obtained from the expression:

$$A(\text{Ti-O}) = \bar{K}_{Ti}\bar{K}_0[2n_0^{Ti} + 5n^0_{Ti}] \quad (5)$$

where n^0_{Ti} is the average co-ordination number of oxygen with respect to titanium.

To estimate n^0_{Ti}, we proceeded as follows:

For a (non-depolymerised) TiO_2 network

$$A(\text{Ti-O}) = \bar{K}_{Ti}\bar{K}_0[n_0^{Ti} + 2n^0_{Ti}] \quad (6)$$

and from the stoichiometry

$$n_0^{Ti} = 2n^0_{Ti}$$

For the depolymerised $2TiO_2.X_2O$ network some oxygens are situated further apart from Ti^{4+} ions owing to the presence of compensating X^+ ions and $n^0{}_{Ti}$ decreases; from stoichiometry it follows that

$$2n_0{}^{Ti} \geqslant 5n^0{}_{Ti}$$

Thus

$$0.4 \leqslant (n_{Ti}{}^0/n_0{}^{Ti}) < 0.5$$

To obtain the *lower limit* of $n_0{}^{Ti}$ we may take $n_{Ti}{}^0 \sim \frac{1}{2}n_0{}^{Ti}$ and write the expression (5) as

$$A(\text{Ti-O}) = 4.5\ \bar{K}_{Ti}\bar{K}_0 n_0{}^{Ti} \qquad (6)$$

This formula leads to average co-ordination numbers of Ti^{4+} with respect to oxygen equal to 6.1 and 6.3 respectively for the potassium and caesium titanates. Bearing in mind the approximations involved, this proves that in the titanate glasses considered, the titanium ion is indeed octahedrally co-ordinated by oxygen, the six oxygens being situated around the titanium ion at an average distance of 1.95 Å.

This result is important as it shows beyond doubt the possibility of an *octahedral co-ordination* for a glass former. The only known case so far is the vitreous tellurium oxide, TeO_2 (containing 10% Li_2O) in which, however, the oxygen octahedra were found to be extremely distorted, four distances Te-O being equal to 1.95 Å and two distances to 2.75 Å [7]. (TeO_2 crystallises in either rutile or brookite form).

In crystalline TiO_2 the TiO_6 octahedra share their corners and edges. In rutile, each octahedron shares two edges; in brookite, three edges; in anatase four edges; each corner always being common to three octahedra. The TiO_6 octahedra are only slightly distorted. In brookite, for example, the shared O-O edges measure 2.50 Å and the non-shared ones 2.76 Å. For an ideal regular TiO_6 octahedron, if Ti-O = 1.95 Å, the O-O edge is equal to 2.76 Å. This second interatomic distance O-O does not appear on the radial distribution curves of alkali titanates; it is, however, perceptible on the *difference curves* (figs. 4 and 5). These curves show the oscillating part $\sum_m K_m 4\pi r^2(\rho_m - \rho_0)$ of the radial distribution function about the parabola of average density ρ_0. The maxima of these curves are very sensitive to the modulations of radial density and enable the unresolved peaks to be located approximately. (The *resolved* maxima of a radial distribution function do not correspond exactly to the maxima of the difference curve as a horizontal tangent on the radial distribution curve evidently corresponds to the value of r for which the slopes of the difference curve and of the parabola of average density are equal and opposite.) The exact position of the two *resolved* peaks has been shown on each difference curve, with the directions of the tangents indicated by arrows.

The maxima at 2.7 and 2.9 Å on figs. 4 and 5 respectively reveal the unresolved distance O-O.

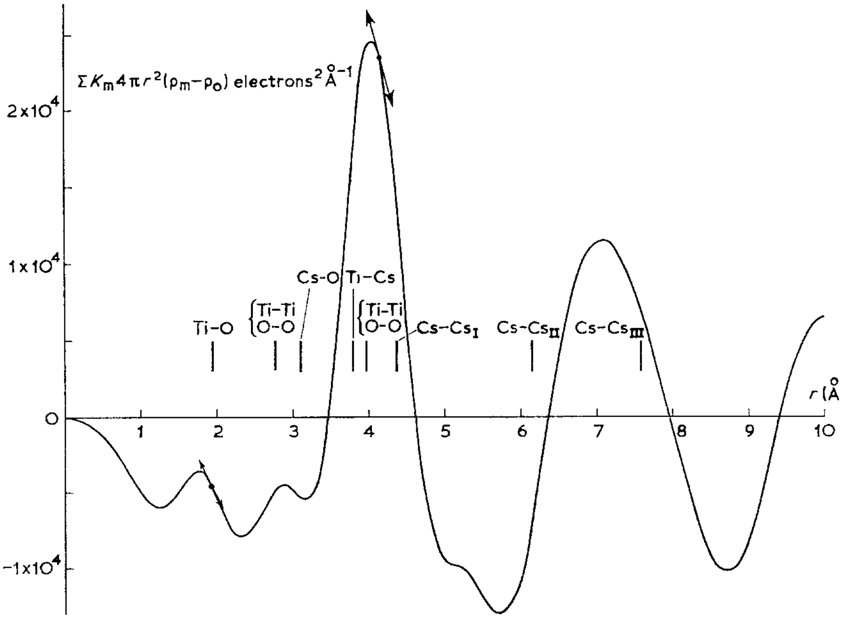

Figure 4 Plot of the difference between the radial distribution function and the average density parabola for vitreous $2TiO_2.K_2O$.

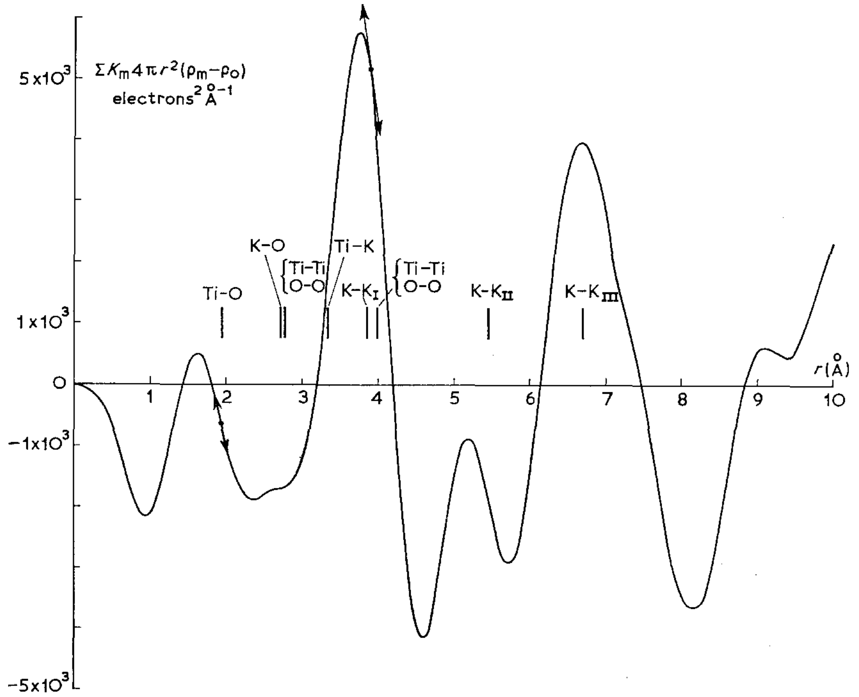

Figure 5 Plot of the difference between the radial distribution function and the average density parabola for vitreous $2TiO_2.Cs_2O$.

When an alkali oxide X_2O is added to TiO_2 to form the $2TiO_2X_2O$ glass, the oxygen ion accompanying two X^+ cations contributes to the depolymerisation of the TiO_2 lattice by opening the edges shared by two octahedra, the partly unsaturated charges on the oxygens involved being compensated by the charges from the cations X^+ which should remain in the vicinity of the corresponding faces.

To investigate further the short range order in these glasses, and in particular the distribution of alkali cations K^+ and Cs^+, an idealised model was used (fig. 6). The cations X^+ are supposed to remain in contact with three oxygens of a face of an octahedron TiO_6 which is linked to other TiO_6 octahedra in a depolymerised TiO_2 network. The possible cationic sites around an octahedron obviously correspond to the corners of a cube. If two cations X^+ are in contact with the same octahedron, then for such pairs the intercationic distances $X\text{-}X_I$, $X\text{-}X_{II}$, $X\text{-}X_{III}$, spaced as 1, $\sqrt{2}$, $\sqrt{3}$, should be found (fig. 6).

These theoretical distances and the Ti-X distances were calculated on the hypothesis of close contact, i.e. taking the X-O distance equal to the sum of the radii of X^+ and O^{2-} ions:

$$K\text{-}O = 1.33 + 1.40 = 2.73\ \text{Å}$$
$$Cs\text{-}O = 1.69 + 1.40 = 3.09\ \text{Å}$$

The calculated Ti-X and X-X distances are inserted in figs. 4 and 5. It can be seen that all the distances indicated correspond systematically to the sequence of maxima of the difference curves. Thus, for $2TiO_2K_2O$ (fig. 4) the (resolved) peak at 3.9 Å is see to be mainly due to the contribution of heavy pairs Ti-K, $K\text{-}K_I$ and Ti-Ti, the

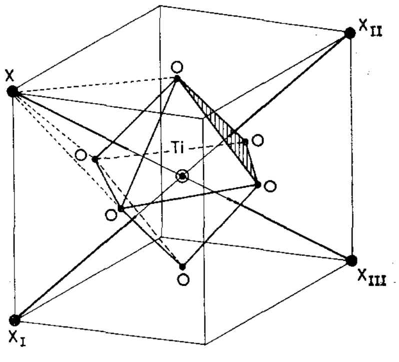

Figure 6 Cationic sites around a TiO_6 idealised octahedron.

peaks at 5.2 and 6.7 Å corresponding to K-K$_{\mathrm{II}}$ and K-K$_{\mathrm{III}}$ distances.

In the case of the $2TiO_2.Cs_2O$ glass (fig. 5), the second (resolved) peak at 4.15 Å is due to the Ti-Cs and Ti-Ti distances. The inflexion at 5.5 Å should correspond to Cs-Cs$_{\mathrm{II}}$ and the maximum at 7.1 Å to the Cs-Cs$_{\mathrm{III}}$ distance. The oxygen-cation contact distance X-O is seen to be close to the first O-O distance and probably enhances the corresponding peak, which is more perceptible for the Cs glass but is displaced towards 2.9 Å.

Thus the simple short range order around an octahedron illustrated in fig. 6 seems to be substantiated, the alkaline cations being distributed on sites corresponding to a cubic arrangement. The succession of the X-X distances is seen to be close to the ideal one ($1 : \sqrt{2} : \sqrt{3}$). This proves, moreover, that the cations are not distributed at random in the network as this would require the successive X-X distance to follow in the ratio 1 : 1.8 : 2.6 as required by the geometry of an irregular assembly of spheres [8].

5. Conclusion

The structural analysis of two alkali titanate glasses shows that the Ti^{4+} ion is octahedrally co-ordinated with respect to oxygen.

Thus the classic geometrical Zachariasen-Warren theory which denies the possibility of an octahedral co-ordination for a glass network former is definitely incorrect, and other approaches should be looked for to explain the vitrification process in oxide systems.

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References

1. P. L. BAYNTON, H. RAWSON, and J. E. STANWORTH, Proc. Fourth Internat. Glass Congr. (Paris) 1956 (Imprimerie Chaix Paris 1957); *Ceram. Abstr.* July (1959) p. 197e.
2. J. RAO, *Phys. Chem. Glasses* **4** (1963) 22; *J. Amer. Ceram. Soc.* **47** (1964) 455.
3. W. B. WHITE, *J. Amer. Ceram. Soc.* **48** (1965) 108.
4. H. RAWSON, "Inorganic Glass Forming Systems" (Academic Press, London, 1967).
5. N. NORMAN, *Acta Cryst.* **10** (1957) 370.
6. B. E. WARREN, H. KRUTTER, and O. MORNINGSTAR, *J. Amer. Ceram. Soc.* **19** (1936) 202.
7. G. W. BRADY, *J. Chem. Phys.* **27** (1957) 300.
8. J. D. BERNAL, "Physics of Simple Liquids" ed. H. N. V. Temperley (North-Holland, Amsterdam, 1968) p. 231.

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