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Mössbauer and DTA Studies of Semiconducting Potassium Vanadate Glasses Containing Iron

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A Mössbauer spectrum of a series of potassium vanadate glasses containing 10 mol% Fe_2O_3 shows a paramagnetic quadrupole doublet, of which isomer shift proves to be smaller than 0.4 mm s^{-1} with respect to metallic iron. This indicates that the individual Fe^{3+} ion is present at the substitutional site of the V^{5+} (and probably V^{4+}) ion constituting a VO_4 tetrahedral unit. An increase in the K_2O content of the potassium vanadate glasses results in a continuous decrease in the glass transition temperature (Tg), ranging from 239 to 200 °C, when the K_2O content is changed from 5 to 30 mol%. This suggests a decrease in the coordination number of the V^{5+} (and V^{4+}) ion from 5 to 4 and a formation of nonbridging oxygen atoms in the VO_4 and FeO_4 tetrahedral units. The formation of nonbridging oxygen atoms in the VO_4 and FeO_4 units is also estimated from a continuous decrease in the quadrupole splitting, suggesting a decrease in the electric field gradient at the iron nucleus and an increase in the symmetry around the Fe^{3+} ion. These results lead to the conclusion that the introduction of the alkali oxide (K_2O) into the V_2O_5 results in a structural change of the V^{5+} (and V^{4+}) ions from VO_5 tetragonal pyramid (or trigonal bipyramid) to VO_4 tetrahedral units.

Electric conducting glasses, i.e., superionic conducting glass and semiconducting glass, have attracted much attention because of the scientific interest in the conduction mechanism as well as the high technological applicability. The electric conductivity of the superionic conducting glasses is known to reach the order of 10^{-2} S cm^{-1},[1–14] which is almost equivalent to that of the crystalline superionic conductor (solid state electrolytes) such as α-AgI and β-Al_2O_3. The high electric conductivity of the superionic conducting glasses is assumed to be due to the "ion migration" of monovalent cations such as Ag^+, Li^+, and Na^+. Comparing the magnitude of the electric conductivity of the superionic conducting glasses to that of the ordinary oxide glasses such as borate and phosphate glasses, which is usually smaller than about 10^{-12} or 10^{-13} S cm^{-1},[15] it is easily understood that the former is extraordinary larger than the latter. Also, the electric conductivity of semiconducting glasses is known to be comparable to that of the superionic conducting glasses.[16–18] The essential difference between the two types of the electric conducting glasses lies in the conduction mechanism. Namely, the electric conductivity of the semiconducting glasses, such as V_2O_5-based glasses studied in the present paper, is known to be due to the electron hopping from the metal ion of lower valence state to the metal ion of higher valence state.[19–21] In the case of the V_2O_5-based glasses, the electric conduction is reported to be performed by a step-by-step electron hopping from the V^{4+} ions, which were produced as a result of thermal decomposition of the V_2O_5 during the sample preparation,[22] to the V^{5+} ions of which number is usually larger than that of the V^{4+}.[19–21] A great number of theoretical treatments of the electric conduction have so far been performed on these semiconducting glasses using a "small polaron hopping theory" proposed by Mott.[23–25] Therefore, it should be noted that the electric conductivity of the semiconducting V_2O_5-based glasses has been studied satisfactorily.

In contrast to the variety of studies performed on the physical properties of vanadate glasses, only a few studies have so far been performed on the structure of the semiconducting V_2O_5-based glasses. Structure of crystalline V_2O_5 has been studied by Byström et al.[26] and by Jansen and Sperlich.[27] They reported that each V^{5+} ion is surrounded by five oxygen atoms making a distorted tetragonal pyramid, which can also be viewed as a distorted trigonal bipyramid, sharing edges and corners to form layers. IR study of several vanadate glasses performed by Dimitriev et al.[28] revealed that the introduction of alkali or alkaline earth oxides, which usually play a role of network modifier, into the V_2O_5 matrix results in a destruction of the vanadate layers followed by a formation of tetrahedral VO_4 units. Dimitriev et al.[28] also elucidated that only the VO_4 units are present in the skeleton of metavanadate glasses, where the molar ratio between the alkali or the alkaline earth oxides and the V_2O_5 is equal to 1. They also revealed that the introduction of other kind of oxides, which play a role of network former, such as SiO_2, B_2O_3, GeO_2, and TiO_2 affects no structural change on the skeleton of the glass matrix originally made of only VO_5 units. In the latter case, the individual network-forming atoms, i.e. Si, B, Ge, and Ti were concluded to be substituted for the fivefold-coordinated V^{5+} (or V^{4+}) ions forming VO_5 units. On the other hand, a neutron diffraction study performed by Wright et al.[29] revealed that the coordination number of vanadium is always 5 in the P_2O_5-, BaO-, and PbO-V_2O_5 glasses irrespective of the glass composition, and that the skeleton of the vanadate glasses is composed of interconnected and distorted VO_5 tetragonal pyramid (or trigonal bipyramid), similarly to the VO_5 units in the crystalline

V_2O_5. Besides the VO_4 and VO_5 units described above, the presence of octahedral VO_6 units has also been proposed, based on the composition dependency of specific gravity.[18,30] Iron-Mössbauer spectroscopy has also been utilized for the structural study of vanadate glasses.[31–34] However, the conclusions obtained so far by the Mössbauer spectroscopy are inconsistent with each other. For example, the coordination number of Fe^{3+} ion is reported to be only six in the case of barium vanadate glass[31] and to be both six and four in the cases of barium or calcium borovanadate[32,33] and sodium vanadate[34] glasses. The conclusions concerning the coordination number of the Fe^{3+} ion reported in those papers seem to be very doubtful because all the isomer shifts, which can be a criterion of octahedral and tetrahedral symmetries, actually indicate the presence of only tetrahedral Fe^{3+} species in those vanadate and borovanadate glasses.[31–34] (All the isomer shifts obtained in those glasses are smaller than 0.4 mm s^{-1} with respect to metallic iron.)

In the light of these reasons, the present Mössbauer and DTA (Differential Thermal Analysis) studies were carried out in order to elucidate the local structure and the structural change, brought about by the introduction of K_2O into the V_2O_5 matrix, of a series of potassium vanadate glasses. Small amounts of Fe_2O_3 were incorporated into the vanadate glasses as a Mössbauer probe. DTA method was utilized in order to know the structural change of the vanadate glasses through the glass transition temperature (T_g), because the T_g is known to reflect the change in the coordination number of network forming atoms and the destruction of the network structure followed by a formation of nonbridging oxygen atoms.[14,35–39]

Experimental

A series of potassium vanadate glasses were prepared by fusing the individual mixtures of commercially available K_2CO_3, V_2O_5, and Fe_2O_3, of a guaranteed reagent grade, at 1000 °C for 1 h in an electric muffle furnace. After the fusion in the ambient atmosphere, each melt in a platinum crucible was immediately quenched with ice-cold water in a beaker. The vanadate glasses were tried to prepare in the compositional ranges of $0 \leqq K_2O \leqq 40$ mol%, 50 mol% $\leqq V_2O_5 \leqq$ 90 mol%, and 5 mol% $\leqq Fe_2O_3 \leqq 20$ mol%. All the glass samples prepared in the present study were almost black in color and completely transparent. Mössbauer and DTA measurements were performed only for the vanadate glasses of which composition is expressed by $xK_2O \cdot (90-x)V_2O_5 \cdot 10Fe_2O_3$ in order to investigate the effect of the alkali oxide (K_2O) content on the structure of the vanadate glasses. Mössbauer measurements were performed by a constant acceleration method at room temperature with a proportional counter and a 1024 channel multichannel analyzer. Cobalt-57 (10 mCi) diffused into a palladium foil was used as the Mössbauer source. As the standard material for the isomer shift, a metallic iron foil enriched with iron-57 was used. The iron foil was also used for the velocity-calibration of the spectrometer. Each Mössbauer spectrum was analyzed into a quadrupole doublet with the same peak intensity and the same linewidth. DTA measurements of the vanadate glasses were performed in the temperature range from room temperature to 550 °C with a heating rate of 5 °C min^{-1}. An Al_2O_3 powder was used as the standard material in the DTA measurements.

Results and Discussion

The glass-forming region for the ternary K_2O–V_2O_5–Fe_2O_3 glass system is shown in Fig. 1, where open and closed circles indicate the formations of glass and non-glassy (devitrified) samples, respectively. It is easily understood from Fig. 1 that the introduction of the Fe_2O_3 into the K_2O–V_2O_5 system results in an extended glass-forming region as compared to the binary K_2O–V_2O_5 system. Extended glass-forming region has also been observed in CuO–V_2O_5–TeO_2 glass system,[18] and in BaO–V_2O_5–TeO_2, P_2O_5–V_2O_5–TeO_2, Fe_2O_3–V_2O_5–TeO_2, and ZnO–V_2O_5–TeO_2 glass systems.[40] On the other hand, reduced glass-forming region has been observed when TiO_2 is introduced into the V_2O_5–TeO_2 system.[40] The change in the glass-forming region will be correlated with the chemical and physical properties of the components, such as nature of the chemical bond, ionic radius, melting point, and viscosity. It is understood from Fig. 1 that the formation of the ternary K_2O–V_2O_5–Fe_2O_3 glasses is limited to a relatively small compositional region. A Mössbauer spectrum of the potassium vanadate glasses measured at room temperature is shown in Fig. 2, which indicates the

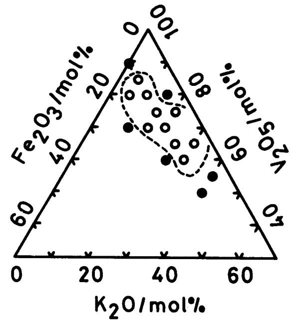

Fig. 1. Glass-forming region for the K_2O–V_2O_5–Fe_2O_3 system.

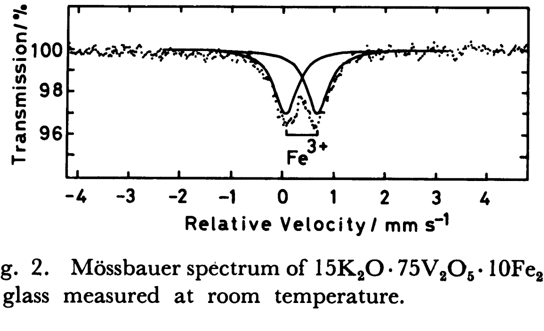

Fig. 2. Mössbauer spectrum of $15K_2O \cdot 75V_2O_5 \cdot 10Fe_2O_3$ glass measured at room temperature.

presence of paramagnetic Fe^{3+} ions of high spin state, since the isomer shift (with respect to metallic iron) of the quadrupole doublet is much larger than 0 mm s^{-1}.[41,42] (In the case of the absorptions due to the Fe^{3+} ions of low spin state, the isomer shift is known to fall to the neighborhood of 0 mm s^{-1}.[41,42]) All the Mössbauer parameters for the vanadate glasses studied in the present paper are summarized in Table 1, from which it is seen that the isomer shifts are located in a small range of 0.35—0.37 mm s^{-1}. As for the coordination number of iron in glasses, earlier works are reviewed by Kurkjian[43] and Coey.[44] Recent works on the structure of glasses are reviewed by Müller-Warmuth and Eckert.[45] Coey suggested that the Fe^{3+} ions are present at the tetrahedral sites in borate and silicate glasses.[44] This is well consistent with the Mössbauer results of a series of borate[14,46–48] and borosilicate[49,50] glasses containing small amounts of Fe_2O_3, performed by the present authors. In those Mössbauer studies,[14,46–50] all the isomer shifts (with respect to metallic iron) proved to lie in a range of 0.22—0.38 mm s^{-1}, and the experimental error for the isomer shift has been estimated to be ±0.01 or 0.02 mm s^{-1}. Judging from the experimental results shown in the reviews on the structure of glasses[43–45] and from the recent Mössbauer results on the structure of glasses performed by the present authors,[14,46–50] the isomer shift of the Fe^{3+} ions is concluded to be smaller than 0.40 mm s^{-1} for the tetrahedral symmetry. On the other hand, octahedrally coordinated Fe^{3+} ions have been observed in several phosphate glasses,[51–53] where all the isomer shifts proved to be larger than 0.42 mm s^{-1}. These experimental results lead to the conclusion that the criterion of the isomer shift for the Fe^{3+} ions with tetrahedral and octahedral symmetries lies at about 0.40 mm s^{-1}. Those symmetries strictly refer to the "distorted" octahedral and "distorted" tetrahedral configurations, since the bond lengths and the bond angles are widely distributed in the amorphous materials such as the glasses. This is well reflected in the magnitude of the linewidth summarized in Table 1, i.e., the linewidth is much larger than that of the ordinary crystalline compounds containing iron.[41,42] Considering all the experimental results described above, the present Mössbauer results, especially the isomer shifts suggest that the Fe^{3+} ions are present at the tetrahedral sites in the alkali vanadate glasses. This conclusion indicates the presence of VO_4 tetrahedral units as well as the FeO_4 units, because all the Mössbauer spectra, e.g. Fig. 2, obtained in the present study indicate the presence of a paramagnetic and homogeneous glass phase. All the Fe^{3+} ions are therefore concluded to be present at the substitutional sites of the V^{5+} (and probably V^{4+}) ions constituting VO_4 tetrahedra, as a constituent of the skeleton of the glass matrix. Similarly to the case of the Fe^{3+} ions incorporated into borate,[14,44,46–48] silicate,[44] and borosilicate[49,50] glasses, it is considered that the Fe^{3+} ions are easily incorporated into the vanadate matrix. The substitution of the iron for the other metal or metalloid ions will easily occur in the high energy and non-equilibrium states where the glass samples are prepared by fusion. It is also concluded that the introduction of the alkali oxide (K_2O in the present study) into the V_2O_5 matrix results in a formation of VO_4 tetrahedral units, instead of the VO_5 tetragonal pyramids (or trigonal bipyramids) which originally constituted the V_2O_5 matrix.[26,27] This conclusion is well consistent with the IR results obtained by Dimitriev et al.[28] They concluded that the introduction of the alkali or alkaline earth oxides into the V_2O_5 matrix results in a formation of VO_4 tetrahedral units. Their conclusion is based on the disappeared vibrational mode, originally observed at 1020 cm^{-1}, of the V=O bond constituting the VO_5 tetragonal pyramid (or trigonal bipyramid).[28] On the other hand, a few Mössbauer studies on the structure of vanadate glasses obtained recently[31–34] suggest that a large number of Fe^{3+} ions are octahedrally present at the interstitial sites, i.e., between the layer structure composed of the VO_5 units. The individual isomer shifts reported in those vanadate glasses are 0.36,[31] 0.35,[34] 0.30,[33] and 0.27—0.29[32] mm s^{-1} with respect to metallic iron. (The isomer shift of 0.36 mm s^{-1} in Ref. 31 was obtained by subtracting 0.26 mm s^{-1} from the isomer shift with respect to sodium nitroprusside.[41,42]) Considering the experimental results obtained in the present study, together with the several Mössbauer results of the structure of several kinds of glasses[14,43–53] and with the reviews on the coordination number of iron in several compounds,[41,42] it should be noted that those isomer shifts[31–34] are actually indicative of the presence of FeO_4 tetrahedral units constituting the skeleton of the glass matrix. Therefore, the conclusion on the structure of the vanadate glasses obtained in those Mössbauer studies,[31–34] i.e. a large number of Fe^{3+} ions are present at the octahedral and interstitial sites (between the layer structure), seems very doubtful.

Table 1. Mössbauer Parameters for K_2O–V_2O_5–Fe_2O_3 Glasses

Composition	δ[a)] mm s^{-1}	Δ[b)] mm s^{-1}	Γ[c)] mm s^{-1}
$5K_2O \cdot 85V_2O_5 \cdot 10Fe_2O_3$	0.37	0.61	0.60
$10K_2O \cdot 80V_2O_5 \cdot 10Fe_2O_3$	0.36	0.63	0.55
$15K_2O \cdot 75V_2O_3 \cdot 10Fe_2O_3$	0.36	0.62	0.53
$20K_2O \cdot 70V_2O_5 \cdot 10Fe_2O_3$	0.37	0.61	0.59
$25K_2O \cdot 65V_2O_5 \cdot 10Fe_2O_3$	0.36	0.59	0.58
$30K_2O \cdot 60V_2O_5 \cdot 10Fe_2O_3$	0.35	0.55	0.67

a) Isomer shift. b) Quadrupole splitting. c) Linewidth.

The composition dependency of the isomer shifts for the Fe^{3+} ions in the vanadate glasses obtained in the present study is shown in Fig. 3. It is seen from Fig. 3 that the isomer shifts are almost constant irrespective of the alkali oxide (K_2O) content, and that the isomer shift shows a slight decrease with the increase in the K_2O content. A drastic decrease in the isomer shifts of the Fe^{3+} ions has already been observed in borate[46–48] and borosilicate[49,50] glasses when the alkali oxide content increases. In those glasses,[46–50] the decrease in the isomer shift of the Fe^{3+} ions, which are present at the substitutional sites of the tetrahedral boron or silicon atoms, was ascribed to the formation of nonbridging oxygen atoms ($—O^-$) in BO_4 and SiO_4 tetrahedral units, because the formation of nonbridging oxygen atoms results in decreased interatomic distances between boron and oxygen or silicon and oxygen atoms. This will cause an increase in the s-electron density at the iron nucleus and the decrease in the isomer shift. The formation of nonbridging oxygen atoms will also affect the degree of the thermal vibration of boron or silicon atoms, and as a result, the increased thermal vibration (second order Doppler effect) will result in the decrease in the isomer shift. In the case of germanate glasses,[37,54] of which network structure is composed of GeO_4 and GeO_6 units, a drastic increase in the isomer shift of Sn^{4+} ions was observed. The increase in the isomer shift of the Sn^{4+} suggests an increased s-electron density at the tin nucleus, brought about by the formation of nonbridging oxygen atoms in GeO_4 tetrahedral units. (In the case of the ^{119}Sn-Mössbauer spectroscopy, an increase in the s-electron density results in the increase in the isomer shift, opposite to the case of the ^{57}Fe-Mössbauer spectroscopy.[41,42]) A slight decrease in the isomer shift shown in Fig. 3 is therefore ascribed to the formation of nonbridging oxygen atoms in the VO_4 tetrahedral units. This conclusion is supported by the remarkable composition dependence of the quadrupole splitting shown in Fig. 4. It is seen from Fig. 4 that the quadrupole splitting shows a distinct decrease when the K_2O content exceeds about 15 mol%. As for the composition dependency of the quadrupole splitting of the Fe^{3+} ions in glasses, distinct decreases in the quadrupole splitting have been observed when the nonbridging oxygen atoms are formed in borate,[46–48] borosilicate,[49,50] and phosphate[52,53] glasses. The decrease in the quadrupole splitting of the Fe^{3+} ions is ascribed to the increased symmetry around the Fe^{3+} ions, because the Fe^{3+} ions of high spin state have a symmetric electron configuration of $3d^5$, and only the electric field gradient brought about by the neighboring atoms or ions primarily affects the quadrupole splitting values. Similar phenomenon has been observed in the germanate glasses containing tin (Sn^{4+}),[37,54] where the nonbridging oxygen atoms are concluded to be formed in GeO_4 tetrahedral units. These considerations lead to the conclusion that the increase in the symmetry around the Fe^{3+} ions constituting the FeO_4 tetrahedral units, observed in the present study, indicates the formation of nonbridging oxygen atoms in the VO_4 tetrahedral units constituting the skeleton of the alkali vanadate glasses, because each Fe^{3+} ion is considered to be present at the substitutional site of the V^{5+} or V^{4+} ion as described above. Therefore, the present Mössbauer results lead to the conclusion that the increase in the K_2O content results in a decrease in the coordination number of vanadium ion from 5 to 4. At the same time, it is also concluded that nonbridging oxygen atoms are formed in some of the VO_4 tetrahedral units. (These Mössbauer results are based on the assumption that the structural change of the V^{5+} or V^{4+} ions, brought about by the introduction of K_2O into the V_2O_5 matrix, is equivalent to that of the Fe^{3+} ions.)

Each DTA curve of the potassium vanadate glasses containing 10 mol% Fe_2O_3 proved to consist of a simple endothermic peak due to glass transition and one or a few exothermic peak(s) due to crystallization. All the glass transition temperatures (T_g) obtained in the present study are shown in Fig. 5, where the T_g values are plotted against the K_2O content of the vanadate glasses. DTA studies on the structure of several glasses have already revealed that

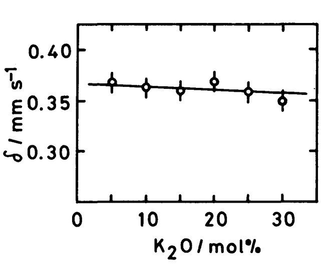

Fig. 3. Composition dependence of the isomer shift (δ) of the Fe^{3+} ions in K_2O–V_2O_5 glasses containing 10 mol% Fe_2O_3.

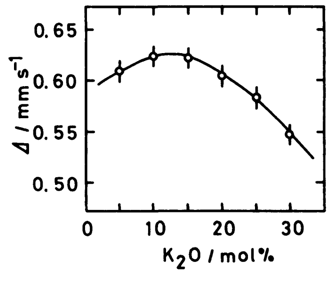

Fig. 4. Composition dependence of the quadrupole splitting (Δ) of the Fe^{3+} ions in K_2O–V_2O_5 glasses containing 10 mol% Fe_2O_3.

T_g shows a close correlation with the change in the coordination number of the network-forming atoms (network former) and with the formation of nonbridging oxygen or fluorine atoms which means a destruction or depolymerization of the network structure.[14,35–38] The T_g, in general, shows a distinct increase when the coordination number of the network former increases. For example, the change in the coordination number of Ge from 4 to 6 is observed as a continuous increase in the T_g in the case of germanate glasses.[35–37] Contrary to this, a formation of nonbridging oxygen is known to cause a decrease in the T_g.[35–37] Considering these results, it is expected that a decrease in the coordination number of the network former, if present, will be observed as a decrease in the T_g. The continuous and distinct decrease in the T_g from 239 to 200 °C observed in the present study, therefore, seems to suggest the gradual decrease in the coordination number of V^{5+} and V^{4+} ions from 5 to 4. This conclusion obtained from the DTA measurements is well consistent with the IR results obtained by Dimitriev et al.[28] All the T_g values obtained in the present study are summarized in Table 2, together with the individual crystallization temperatures (T_c). It is understood from Table 2 that the T_c is higher than the T_g by 20—45 °C. In Table 2, only one crystallization temperature (the lowest one) is given for each glass sample. Considering the Mössbauer results (Figs. 3 and 4) obtained in the present study together with the previous DTA results described above,[35–37] the decrease in the T_g shown in Fig. 5 (and Table 2) is ascribed to the formation of nonbridging oxygen atoms in the VO_4 and FeO_4 tetrahedral units as well as the decrease in the coordination number of the V^{5+} and V^{4+} ions from 5 to 4. The formation of nonbridging oxygen atoms will become pronounced when the alkali oxide content of the vanadate glasses is high.

Table 2. Glass Transition and Crystallization Temperatures of K_2O–V_2O_5–Fe_2O_3 Glasses

Composition	T_g[a)]/°C	T_c[b)]/°C
$5K_2O \cdot 85V_2O_5 \cdot 10Fe_2O_3$	239	264
$10K_2O \cdot 80V_2O_5 \cdot 10Fe_2O_3$	232	255
$15K_2O \cdot 75V_2O_3 \cdot 10Fe_2O_3$	232	252
$20K_2O \cdot 70V_2O_5 \cdot 10Fe_2O_3$	224	253
$25K_2O \cdot 65V_2O_5 \cdot 10Fe_2O_3$	220	265
$30K_2O \cdot 60V_2O_5 \cdot 10Fe_2O_3$	200	240

a) Glass transition temperature. b) Crystallization temperature.

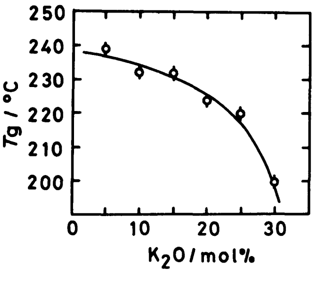

Fig. 5. Composition dependence of the glass transition temperature (T_g) of K_2O–V_2O_5 glasses containing 10 mol% Fe_2O_3.

All the experimental results obtained in the present study suggest that the introduction of alkali oxide into V_2O_5 matrix results in a structural change from VO_5 tetragonal pyramid (or trigonal bipyramid) to VO_4 tetrahedra. In addition to the formation of the VO_4 tetrahedra, a formation of nonbridging oxygen atoms is also concluded in the VO_4 tetrahedral units especially when the alkali oxide content is high. Each Fe^{3+} ion is concluded to be present at the substitutional site of the V^{5+} or V^{4+} ion constituting the VO_4 tetrahedral unit.

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