Structural Studies on Alkaline Earth Vanadate Glasses (Part 1) — IR Spectroscopic Study —

Satoshi HAYAKAWA, Toshinobu YOKO and Sumio SAKKA
Institute for Chemical Research, Kyoto University, Gokasho, Uji-shi, Kyoto 611

The structure of alkaline earth vanadate glasses of the compositions, \( xMO \cdot (100-x)V_2O_5 \) (M=Mg, Ca, Sr, Ba, \( x=30, 40, 45, 50, 55 \)), has been investigated by means of IR spectroscopy with reference to various crystalline alkaline earth vanadates structurally known. It is found that the structure of alkaline earth vanadate glasses is very similar to each other and mainly consists of VO\(_4\)-tetrahedra which form either (VO\(_3\))\(_n\)-single chains as found in Sr(VO\(_3\))\(_2\) and Ba(VO\(_3\))\(_2\) crystals or the three dimensional arrangement of the corner-sharing branched VO\(_4\)-tetrahedral groups as found in molten and amorphous VO\(_2\)O\(_5\). It is stressed that the glass network of the V\(_2\)O\(_5\)-rich glasses, 30MO·70V\(_2\)O\(_5\), also mainly consists of VO\(_4\)-tetrahedra.

Key-words: Structure of alkaline earth vanadate glasses, Infrared spectra, VO\(_4\)-tetrahedra

1. Introduction

Amorphous and crystalline materials containing V\(_2\)O\(_5\) exhibit semiconducting properties and catalytic activities for the oxidation of hydrocarbons in chemical industry. Electrical conductivity of vanadate glasses has been reported to be due to a small polaron hopping.\(^1,2\) As for V\(_2\)O\(_5\)-based catalysts, it is well-known that the surface V=O species are active sites for the selective oxidation of hydrocarbons.\(^3\) Various oxides are used as promoters for the V\(_2\)O\(_5\)-catalysts to improve the catalytic properties. However, little is known about the effect of the promoters on the active sites.

For a better understanding of these phenomena, information on the local structure of vanadium ions is needed. Although the structure of vanadate glasses has been investigated by various spectroscopic and diffraction techniques, e.g., X-ray RDF,\(^3\) neutron RDF,\(^7\) IR,\(^8\)-10 Raman,\(^11\) EXAFS,\(^12\) XANES,\(^14\),15 and NMR,\(^15\),16 only a few systematic studies have been carried out especially to understand the compositional change of the glass structure.

In this work, IR absorption spectra measurements were performed on alkaline earth vanadate glasses of the compositions, \( xMO \cdot (100-x)V_2O_5 \) (M=Mg, Ca, Sr, Ba, \( x=30, 40, 45, 50, 55 \)) in order to examine the glass structure. Especially, the effects of the kind of alkaline earth element and the MO content on the structure of the glasses were discussed.

2. Experimental

2.1 Sample preparation

Four series of alkaline earth vanadate glasses of the compositions, \( xMO \cdot (100-x)V_2O_5 \) (M=Mg, Ca, Sr, Ba, \( x=30, 40, 45, 50, 55 \)) were prepared using reagent-grade V\(_2\)O\(_5\), MgO, CaCO\(_3\), SrCO\(_3\), BaCO\(_3\) chemicals supplied by Nacalai Tesque. Starting materials were well mixed and then melted in a Pt-5% Au crucible in an electric furnace at temperatures of 950 to 1100°C. The melts were poured onto a brass plate and immediately pressed by another one. For \( xMgO \cdot (100-x)V_2O_5 \) (\( x=30, 40, 50 \)), 50CaO·50V\(_2\)O\(_5\) and 55SrO·45V\(_2\)O\(_5\), the crucible containing a small quantity of melt was directly soaked into ice water to cool down more quickly. The melting conditions for all the vanadate glasses prepared are shown in Table 1.

Table 1. Preparation Conditions for Glass Samples, \( V^{4+}/V_{\text{Total}} \) and Density

<table>
<thead>
<tr>
<th>Glass sample</th>
<th>Melting temperature / °C</th>
<th>Time / min</th>
<th>( V^{4+}/V_{\text{Total}} ) / %</th>
<th>Density / g cm(^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>50MgO·50V(_2)O(_5)</td>
<td>1100</td>
<td>10</td>
<td>-</td>
<td>2.83</td>
</tr>
<tr>
<td>40MgO·60V(_2)O(_5)</td>
<td>950</td>
<td>10</td>
<td>2.5</td>
<td>2.88</td>
</tr>
<tr>
<td>30MgO·70V(_2)O(_5)</td>
<td>950</td>
<td>10</td>
<td>4.3</td>
<td>2.89</td>
</tr>
<tr>
<td>50CaO·50V(_2)O(_5)</td>
<td>1070</td>
<td>10</td>
<td>3.3</td>
<td>3.07</td>
</tr>
<tr>
<td>40CaO·60V(_2)O(_5)</td>
<td>950</td>
<td>10</td>
<td>2.5</td>
<td>3.00</td>
</tr>
<tr>
<td>30CaO·70V(_2)O(_5)</td>
<td>950</td>
<td>10</td>
<td>5.0</td>
<td>3.03</td>
</tr>
<tr>
<td>55SrO·45V(_2)O(_5)</td>
<td>1070</td>
<td>10</td>
<td>-</td>
<td>3.53</td>
</tr>
<tr>
<td>50SrO·50V(_2)O(_5)</td>
<td>950</td>
<td>10</td>
<td>1.9</td>
<td>3.55</td>
</tr>
<tr>
<td>45SrO·55V(_2)O(_5)</td>
<td>950</td>
<td>10</td>
<td>2.4</td>
<td>3.50</td>
</tr>
<tr>
<td>40SrO·60V(_2)O(_5)</td>
<td>950</td>
<td>10</td>
<td>2.6</td>
<td>3.40</td>
</tr>
<tr>
<td>30SrO·70V(_2)O(_5)</td>
<td>950</td>
<td>10</td>
<td>4.7</td>
<td>3.27</td>
</tr>
<tr>
<td>20SrO·80V(_2)O(_5)</td>
<td>950</td>
<td>10</td>
<td>5.0</td>
<td>3.17</td>
</tr>
<tr>
<td>50BaO·50V(_2)O(_5)</td>
<td>950</td>
<td>10</td>
<td>2.1</td>
<td>3.93</td>
</tr>
<tr>
<td>45BaO·55V(_2)O(_5)</td>
<td>950</td>
<td>10</td>
<td>1.6</td>
<td>3.86</td>
</tr>
<tr>
<td>40BaO·60V(_2)O(_5)</td>
<td>950</td>
<td>10</td>
<td>2.4</td>
<td>3.74</td>
</tr>
<tr>
<td>30BaO·70V(_2)O(_5)</td>
<td>950</td>
<td>10</td>
<td>4.2</td>
<td>3.60</td>
</tr>
</tbody>
</table>
Crystalline alkaline earth vanadates, $M_3(VO_4)_2$, $M_2V_2O_7$, $M(VO_3)_2$ ($M=$Ca, Sr, Ba) were used as reference materials. The procedures of preparation of these crystalline vanadates are described in our previous papers.17),18)

2.2 Density measurements
The density of the glass samples was determined at room temperature (24°C) by the Archimedes method using kerosine as an immersion liquid.

2.3 Chemical analysis
The $V^{4+}$ and total V contents of glass samples were determined by a redox titrimetry using KMnO$_4$ and (NH$_4$)$_2$Fe(SO$_4$)$_2$ solution (JIS G1221).

2.4 IR absorption spectra measurements
The IR absorption spectra of the glass samples and crystalline alkaline earth vanadates were measured on discs of glass-KBr and crystal-KBr utilizing a Shimadzu FT-IR 8100 spectrophotometer.

3. Results
All glass samples were confirmed to be amorphous by their X-ray diffraction patterns.

A $V^{4+}/V_{Total}$ ratio and the density of glass samples are shown in Table 1. It is seen that both the values change depending on the MO (M=Mg, Ca, Sr and Ba) content. For instance, the $V^{4+}/V_{Total}$ ratio increases with decreasing MO content with some exceptions. The density increases with increasing atomic weight of alkaline earth metal. The influence of $V^{4+}$ ions on the density is considered negligible in the following discussion, because the percentage of $V^{4+}$ ions is not more than 5% as seen in Table 1.

IR spectra of vanadate glasses of the compositions, 50MgO·50V$_2$O$_5$, 50CaO·50V$_2$O$_5$, xSrO·(100-x)V$_2$O$_5$ ($x=55, 50$) and 50BaO·50V$_2$O$_5$ are shown in Figs. 1(a), (b), (c) and (d), respectively, together with the spectra of structurally-known crystalline compounds such as Mg$_3$(VO$_4$)$_2$, Mg$_2$V$_2$O$_7$, Mg(VO$_3$)$_2$, V$_2$O$_5$, Ca$_2$V$_2$O$_7$, Ca(VO$_3$)$_2$, Sr$_3$(VO$_4$)$_2$, Sr$_2$V$_2$O$_7$, Sr(VO$_3$)$_2$, Ba$_3$(VO$_4$)$_2$, Ba$_2$V$_2$O$_7$, Ba(VO$_3$)$_2$. Table 2 lists the infrared absorption bands ranging from 400 to 1200 cm$^{-1}$ of these crystals. The analysis of spectra of these glass samples has been carried out by comparison with structurally-known compounds.

Figures 2(a), (b), (c) and (d) show the IR spectra of xMO·(100-x)V$_2$O$_5$ ($x=30, 40, 45, 50, 55, M=Mg, Ca, Sr, Ba$) glasses. Table 3 lists the infrared absorption bands ranging from 400 to 1200 cm$^{-1}$ of these glasses.

In Fig. 2(a) the absorption band at 1005 cm$^{-1}$ becomes distinct as a shoulder with decreasing MgO content. The absorption band at 930 cm$^{-1}$ in 50MgO·50V$_2$O$_5$ glass shifts to high wavenumbers and becomes intense with decreasing MgO content. The position and intensity of the absorption bands in the 500–840 cm$^{-1}$ region change with MgO content.

In Fig. 2(b) the absorption band at 955 cm$^{-1}$ in 50CaO·50V$_2$O$_5$ glass becomes intense and shifts to high wavenumbers in 50SrO·50V$_2$O$_5$ glass. The absorption band at 645–668 cm$^{-1}$ is observed in all spectra, but this band broadens with decreasing SrO content.

In Fig. 2(d) the spectral profiles of IR spectra of
Structural Studies on Alkaline Earth Vanadate Glasses (Part 1) — IR Spectroscopic Study —

**Table 2. Position of Peaks in the Infrared Absorption Spectra in Alkaline Earth Vanadate Crystals**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Absorption peak position / cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orthovanadates</td>
<td></td>
</tr>
<tr>
<td>Mg₂(VO₃)₆</td>
<td>913 864 831 693 477 434</td>
</tr>
<tr>
<td>Sr₂(VO₃)₆</td>
<td>874 815 740 580</td>
</tr>
<tr>
<td>Ba₂(VO₃)₆</td>
<td>846 811 746</td>
</tr>
<tr>
<td>Band assignment</td>
<td>(v_1), (v_2), (v_3)</td>
</tr>
<tr>
<td>Pyrovanadates</td>
<td></td>
</tr>
<tr>
<td>Mg₆V₂O₁₄</td>
<td>982 913(s) 874(s) 844(s) 815 668 579 532 439</td>
</tr>
<tr>
<td>Ca₆V₂O₁₄</td>
<td>937 890 843 792 789 671 578 510(s) 441 405</td>
</tr>
<tr>
<td>Sr₆V₂O₁₄</td>
<td>929 912 895 875 846 816 747 727 584 416 407</td>
</tr>
<tr>
<td>Ba₆V₂O₁₄</td>
<td>916 895 870 841 825 811 744 722 565 409 402</td>
</tr>
<tr>
<td>Band assignment</td>
<td>(v(V=O)), (v_1(VO_3)), (v_2(VO_3)), (v_3(VO_3)), (v(V=O))</td>
</tr>
<tr>
<td>Metavanadates</td>
<td></td>
</tr>
<tr>
<td>Mg₂(VO₃)₆</td>
<td>913(s) 873 661 556 436</td>
</tr>
<tr>
<td>Ca₂(VO₃)₆</td>
<td>970 853 616 609</td>
</tr>
<tr>
<td>Sr₂(VO₃)₆</td>
<td>953 945 920 897 853 710 683 510 445</td>
</tr>
<tr>
<td>Ba₂(VO₃)₆</td>
<td>953 928 899 876 845 816 702 677 509 442 404</td>
</tr>
<tr>
<td>(V_2O_5)</td>
<td>1021 982 831 618 516 481 418(s)</td>
</tr>
<tr>
<td>Band assignment</td>
<td>(v(V=O)), (v_1(VO_3)), (v_2(VO_3)), (v_3(VO_3)), C.V. (v(V=O))</td>
</tr>
</tbody>
</table>

s: shoulder, C.V.: combination vibration of \((VO_3)_n\)-single chain

---

Fig. 2. IR spectra of alkaline earth vanadate glasses. (a) \(x\)MgO·(100–\(x\))V₂O₅ \((x=30, 40, 50)\), (b) \(x\)CaO·(100–\(x\))V₂O₅ \((x=30, 40, 50)\), (c) \(x\)SrO·(100–\(x\))V₂O₅ \((x=30, 40, 45, 50, 55)\), (d) \(x\)BaO·(100–\(x\))V₂O₅ \((x=40, 45, 50)\)

\(x\)BaO·(100–\(x\))V₂O₅ \((x=40, 45, 50)\) glasses are very similar to those of strontium vanadate glasses having the same MO content. The absorption band at 903–908 cm⁻¹ is observed and shifts to higher wavenumbers and at the same time becomes more intense with decreasing BaO content. The absorption band at 644–667 cm⁻¹ broadens with decreasing BaO content. In 40BaO·60V₂O₅ glass the absorption band at 953 cm⁻¹ is observed as a shoulder on the higher wavenumber side of the broad absorption band at 908 cm⁻¹.

4. Discussion

4.1 Molar volume

A molar volume of crystalline compounds is a measure of the coordination state of a particular
atom.\textsuperscript{19)} This is also the case for glasses. The molar volume, $V_m$, of the vanadate glasses obtained from the density data is plotted against the MO content in Fig. 3. For comparison, the molar volume of alkaline earth metavanadate crystals are also shown. It is clearly seen that the molar volume increases almost linearly with decreasing MO content and takes almost the same value irrespective of the kind of M$^2+$ in those glasses except for $x$BaO·(100$-x$)V$_2$O$_5$ ($x>30$). Such a behavior suggests that the structural units contained in these glasses are basically the same, e.g., VO$_4$ or VO$_5$. The partial molar volumes of V$_2$O$_5$ in 50BaO·50V$_2$O$_5$ glass and Ba(VO$_3$)$_2$ crystal are very close to each other and larger than those of other alkaline earth metavanadate glasses and crystals. It follows that the 50BaO·50V$_2$O$_5$ glass is structurally very similar to the corresponding metavanadate crystal in which V$^5+$ is tetrahedrally coordinated by four oxygens to form (VO$_3$)$_n$-single chains and Ba$^{2+}$ is coordinated by a large number of oxygens, eleven or twelve. Accordingly, a positive deviation from the linearity observed for $x$BaO·(100$-x$)V$_2$O$_5$ glasses possibly arises from the very large coordination number of Ba$^{2+}$ due to its large ionic radius. The molar volumes of 50MO·50V$_2$O$_5$ (M=Ca, Sr, Ba) glasses are slightly larger than those of corresponding metavanadate crystals as expected. It is noteworthy to point out that the molar volume of crystalline Mg(VO$_3$)$_2$ is by far smaller than that of corresponding glass, indicating that the network structure of these glasses does not contain (V$_2$O$_8$)$_n$-zigzag chains consisting of edge-shared VO$_6$-octahedra (Mg(VO$_3$)$_2$).\textsuperscript{20)}

One more interesting thing to be mentioned is that the partial molar volume of V$_2$O$_5$ in these glasses is estimated as 61.3 cm$^3$·mol$^{-1}$ from the linearity in Fig. 3 except for $x$BaO·(100$-x$)V$_2$O$_5$ glasses, which is much larger than 54.2 cm$^3$·mol$^{-1}$ for V$_2$O$_5$ crystal, but is in fair agreement with 61.4 cm$^3$·mol$^{-1}$ obtained for amorphous V$_2$O$_5$ prepared by the splat quenching method, in which branched VO$_4$-tetrahedra are the major structural units.\textsuperscript{21)} This again confirms that the structural units in the glass network are definitely different from VO$_5$-trigonal bipyramids as found in V$_2$O$_5$ crystal. The more detailed discussion will be made later on.
4.2 Band assignments of IR spectra of alkaline earth vanadate crystals

We had better mention the IR band assignments of these alkaline earth vanadate crystals, because not all of them have been reported.

4.2.1 Crystalline orthovanadates

In $\text{M}_2\text{(VO}_3\text{)}_2$ ($\text{M} = \text{Mg, Sr, Ba}$) crystals the absorption bands ranging from 693 to 913 cm$^{-1}$, and the bands at 434–580 cm$^{-1}$ may be assigned to ($v_5$, $v_1$) and $v_4$ vibrations due to VO$_5^{2-}$-tetrahedra, respectively. These absorption bands however are not clearly observed in the IR spectra of alkaline earth vanadate glasses due to overlapping as seen from Figs. 2(a)–(d).

4.2.2 Crystalline pyrovanadates

$\text{Sr}_2\text{V}_2\text{O}_7$ and $\text{Ba}_2\text{V}_2\text{O}_7$ crystals consist of the identical structural units, i.e., $\text{V}_2\text{O}_7^{4-}$ [23,24]. The band assignments of the IR spectra of these crystals have been already carried out by Baran et al. [25] and Botto et al. [26]. They reported that in $\text{Sr}_2\text{V}_2\text{O}_7$ crystal the bands at 929, 912, 875 and 846 cm$^{-1}$ were assigned to the asymmetric stretching vibration of VO$_5$(vs (VO$_5$)), the bands at 895 and 816 cm$^{-1}$ to the symmetric stretching vibration of VO$_5$(vs (VO$_5$)) due to V$_2$O$_7^{4-}$, the bands at 747 and 727 cm$^{-1}$ to the asymmetric stretching vibration of the V–O–V bonds ($v_3$ (VOV)), the band at 584 cm$^{-1}$ to the symmetric stretching vibration of V–O–V bonds ($v_2$ (VOV)) and the bands at 416 and 407 cm$^{-1}$ to the bending mode of VO$_5$($\delta$(VO$_5$)). In $\text{Ba}_2\text{V}_2\text{O}_7$ crystal the band at 916 cm$^{-1}$ is assigned to the symmetric stretching vibration, $v_1$(VO$_5$), the bands at 985, 870, 841, 825 and 811 cm$^{-1}$ to the asymmetric stretching vibration, $v_3$ (VO$_5$), the bands at 744 and 722 cm$^{-1}$ to the asymmetric stretching vibration, $v_3$ (VOV), the band at 565 cm$^{-1}$ to the symmetric stretching vibration, $v_2$ (VOV) and the bands at 409 and 402 cm$^{-1}$ to the bending mode, $\delta$(VO$_5$) due to V$_2$O$_7^{4-}$.

With reference to the band assignments of the IR spectra of $\text{Sr}_2\text{V}_2\text{O}_7$ and $\text{Ba}_2\text{V}_2\text{O}_7$ crystals, the absorption bands of $\text{Mg}_2\text{V}_2\text{O}_7$ and $\text{Ca}_2\text{V}_2\text{O}_7$ crystals can be assigned as follows. In $\text{Mg}_2\text{V}_2\text{O}_7$ crystal the bands at 982–815 cm$^{-1}$ are assigned to the stretching vibration, $\nu$(VO$_5$), the band at 668 cm$^{-1}$ to the asymmetric stretching vibration, $\nu_3$ (VOV), the band at 579 cm$^{-1}$ to the symmetric stretching vibration, $\nu_4$ (VO) and the bands at 532 and 439 cm$^{-1}$ to the bending mode, $\delta$(VO$_3$) due to V$_2$O$_4^{2-}$. The results are compatible with the assignments by Dimitrov and Dimitriev [12].

Similarly, in $\text{Ca}_2\text{V}_2\text{O}_7$ crystal the bands at 780–937 cm$^{-1}$ are assigned to the stretching vibration, $\nu$(VO$_5$), the band at 671 cm$^{-1}$ to the asymmetric stretching vibration, $\nu_3$ (VOV), the band at 578 cm$^{-1}$ to the symmetric stretching vibration, $\nu_4$ (VO) and the bands at 510, 441 and 405 cm$^{-1}$ to the bending mode, $\delta$(VO$_3$) due to V$_2$O$_4^{2-}$. The results are also compatible with the assignments by Dimitrov and Dimitriev [12].

4.2.3 Crystalline metavanadates

Since $\text{Mg(VO}_3\text{)}_2$ and $\text{Ca(VO}_3\text{)}_2$ crystals contain different structural units, that is, VO$_6$-octahedra and VO$_5$-trigonal bipyramids (tpb’s), respectively, their IR spectra are not similar to each other as seen from Figs. 1(a) and (b). On the other hand, the IR spectral profile of $\text{Ca(VO}_3\text{)}_2$ crystal is very similar to that of $\text{V}_2\text{O}_5$ crystal as in Fig. 1(b), reflecting the similarity of structural unit (VO$_5$-tpb’s) between those two crystals. Referring to the IR band assignments of $\text{V}_2\text{O}_5$ crystal [28], the absorption band at 970 cm$^{-1}$ for $\text{Ca(VO}_3\text{)}_2$ crystal is assigned to the stretching vibration of VO$_6$($\nu$(VO$_6$)) due to VO$_6$-tpb’s having two non-bridging oxygens, the band at 853 cm$^{-1}$ to the asymmetric stretching vibration of the V–O–V bonds ($v_3$ (VOV)) and the band at 609 cm$^{-1}$ to the bending mode of VO$_2$($\delta$(VO$_2$)).

As mentioned above, the IR spectrum of Mg (VO$_3$)$_2$ crystal is different in the shape from $\text{V}_2\text{O}_5$ and $\text{Ca(VO}_3\text{)}_2$ crystals because of the overlapping of several broad absorption peaks and the disappearance of the high frequency band around 970–1020 cm$^{-1}$. This may result from the fact that in Mg (VO$_3$)$_2$ crystal the (V=O)$_2$-zigzag chains come closer to each other to form VO$_6$-octahedra rather than VO$_5$-tpb’s, although the sixth V–O bond (2.67 Å) is much longer than the shortest one (1.66 Å). Taking this into account, the absorption bands at 913 (s) and 873 cm$^{-1}$ may be also assigned to the stretching vibration, $\nu$(VO$_6$) due to VO$_6$-octahedra having two non-bridging oxygens, the band at 661 to the asymmetric stretching vibration, $v_3$ (VOV), the band at 556 cm$^{-1}$ to the symmetric stretching vibration, $v_1$ (VOV) and the band at 436 cm$^{-1}$ to the bending mode of VO$_2$($\delta$(VO$_2$)).

$\text{Sr(VO}_3\text{)}_2$ and $\text{Ba(VO}_3\text{)}_2$ crystals consist of the same structural units, VO$_4$-tetrahedra and the same vanadate group, (VO$_3$)$_n$-single chains. Therefore, their IR spectral profiles are very similar. Referring to the IR band assignments of monovalent metavanadate crystals having the same structure as $\text{Sr(VO}_3\text{)}_2$ and $\text{Ba(VO}_3\text{)}_2$ crystals, the absorption bands at 928–953 cm$^{-1}$ are assigned to the symmetric stretching vibration of VO$_6$($\nu_3$(VO$_6$)) and the asymmetric stretching vibration of VO$_2$($\nu_3$(VO$_2$)) due to (VO$_3$)$_n$-single chains, respectively. The bands at 816–853 cm$^{-1}$ are assigned to the asymmetric vibration of V–O–V bonds ($\nu_4$ (VOV)), the intense and broad absorption bands at 677–683 cm$^{-1}$ to the combination vibration of (VO$_3$)$_n$-single chains, [29,30] the bands at 510 and 509 cm$^{-1}$ to the symmetric stretching vibration of V–O–V bonds ($v_3$ (VOV)) and the bands at 404–445 cm$^{-1}$ to the bending mode, $\delta$(VO$_2$).

In crystalline $\text{Sr(VO}_3\text{)}_2$ and $\text{Ba(VO}_3\text{)}_2$ two crystallographically inequivalent vanadium sites are tetrahedrally surrounded by four oxygens; in site 1, one V–O bond length is very short at 1.61 Å and three
V–O bond lengths are not the same at 1.77, 1.80 and 1.98 Å and in site 2, two sets of equal V–O bond lengths are at 1.72 and 1.84 Å. Accordingly, it seems that the highest frequency band at 953 cm⁻¹ of crystalline Ba(VO₃)₂ is originated from the shortest V–O bond of a VOₓ⁻tetrabedron in site 1. As can be seen in Table 2, in crystalline alkaline earth vanadates, the highest frequency bands shift toward high wavenumbers with decreasing number of non-bridging oxygen atoms bound to a vanadium and increasing oxygen coordination number of a vanadium atom in the order, M₂V₂O₇ (M=Ca, Sr, Ba) (916–937 cm⁻¹) < Ba(VO₃)₂ (953 cm⁻¹) < Ca(VO₃)₂ (970 cm⁻¹) < V₂O₅ (1020 cm⁻¹). It is therefore possible to assign the IR bands of alkaline earth vanadate crystals are plotted against the shortest V–O bond length in Fig. 4. It is obvious that the positions of the highest frequency bands shift to high wavenumbers with decreasing shortest V–O bond length.

4.3 Structure of alkaline earth vanadate glasses based on the IR spectra

Referring to the preceding band assignments made on the IR spectra of various crystalline alkaline earth vanadates, the structure of four series of alkaline earth vanadate glasses with different compositions is discussed in this section. As seen from Figs. 1(a)–(d) and Table 3, the IR spectra of 50SrO·50V₂O₅ and 50BaO·50V₂O₅ glasses are very similar in both shape and peak position to those of corresponding crystalline metavanadates but different from those of other crystalline vanadates, while the shape of IR spectra of 50MgO·50V₂O₅ and 50CaO·50V₂O₅ resemble none of corresponding crystalline vanadates but rather Sr(VO₃)₂. This suggests that the structure of all these metavanadates glasses is basically similar to that of crystalline Sr(VO₃)₂ and Ba(VO₃)₂ both of which consist of (VO₃)ₙ single chains containing only VO₄-tetrahedra as stated above. It is therefore possible to assign the IR bands of 50MO·50V₂O₅ glasses with reference to crystalline Sr(VO₃)₂ and Ba(VO₃)₂.

The following four or five bands are noticeable for the alkaline earth vanadates except magnesium vanadates. The strongest and second strongest bands at 878–903 and 952–955 cm⁻¹ are assigned to the asymmetric (νas(VO₅)) and symmetric (νs(VO₅)) stretching vibrations of VOₓ in VOₓ-tetrabedra composing (VOₓ)ₙ single chains. The latter band reflects the V–O double bond character as mentioned above. The band around 800 and 540 cm⁻¹ are assigned to the asymmetric (νas(V=O)) and symmetric (νs(V=O)) stretching vibrations of V=O–V bond in corner-sharing VOₓ-tetrabedra. Special emphasis has to be placed to the broad and strong band at 635–645 cm⁻¹, because in crystalline vanadates this kind of band appears only when (VOₓ)ₙ single chains consisting of corner-sharing VOₓ-tetrabedra are present.

According to Table 3, a decrease in MO content does not alter essentially the IR spectra of MO·V₂O₅ glass systems although slight changes in peak position and intensity with the composition are observed. This implies that in MO·V₂O₅ glasses the major structural units are basically the same, in this case VOₓ-tetrabedra, independent of the composition and the kinds of M in good agreement with the discussion on the partial molar volume of V₂O₅ in these glasses in the Section 4.1. The present result based on the IR spectroscopy is also compatible with the previous findings by the X-ray RDF method that the corner-sharing branched VOₓ-tetrabedra are the major structural units for both molten V₂O₅ and amorphous V₂O₅ prepared by splat quenching.

On the contrary, several researchers have experimentally recognized the presence of VOₓ-trigonal bipyramids as major structural units based on the absorption band at 1000–1020 cm⁻¹ especially in the V₂O₅-rich glasses, which is inconsistent with the present result. It is quite probable that such an erroneous conclusion may have been drawn from the use of glass samples which were attacked by moisture in ambient atmosphere during the measurements, preparation or preservation, because vanadate glasses are subject to moisture attack to form a compound containing VO₅ units as in VO₅(OH) and V₂O₅·H₂O. In fact, the present authors also observed pronounced effects of moisture attack on the IR spectra of magnesium vanadate glasses as shown in Fig. 5. The absorption bands are listed in Table 4. It is found that the new absorption bands appear at 1005, 989, 804, 742, 589, 538 cm⁻¹ after moisture attack, most of which agree with the bands of amorphous V₂O₅ (probably hydrated), V₂O₅ gel and crystalline V₂O₅. These experimental results indicate that unless measurements are completed within a short time after sample preparation or in dry atmosphere, the IR spectra change drastically due to moisture attack. Therefore, a special care must be...
Structural Studies on Alkaline Earth Vanadate Glasses (Part 1) —— IR Spectroscopic Study ——

Table 4. Position of Peaks in the Infrared Absorption Spectra in Magnesium Vanadate Glasses

<table>
<thead>
<tr>
<th>Composition</th>
<th>Absorption peak position / cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>40MgO-60V₂O₅ glass</td>
<td>1005(s) 963 840(s) 644</td>
</tr>
<tr>
<td>40MgO-60V₂O₅ glass*</td>
<td>989(s) 965 849 808 746 589 538</td>
</tr>
<tr>
<td>30MgO-70V₂O₅ glass</td>
<td>1005(s) 968 848(s) 746 536</td>
</tr>
<tr>
<td>30MgO-70V₂O₅ glass*</td>
<td>988(s) 968 848 804 742 589 538</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Band assignment</th>
<th>V(VO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>V(VO₃)</td>
</tr>
<tr>
<td></td>
<td>V₅(VO₃)</td>
</tr>
<tr>
<td></td>
<td>V₅(VOV)</td>
</tr>
<tr>
<td></td>
<td>C. V.</td>
</tr>
<tr>
<td></td>
<td>V(VOV)</td>
</tr>
</tbody>
</table>

s: shoulder, *: after hydration, C. V.: combination vibration of (VO₃)ₙ-single chain

Although in V₂O₅-rich glasses the absorption bands at 964–968 cm⁻¹ and 900–903 cm⁻¹ are also observed, these bands are attributable to v₅(VO₂) and v₅(VO₃) not only in VO₄-tetrahedral units constructing (VO₃)ₙ-single chains but also in VO₅-tbp’s as found in crystalline Ca(VO₃)₂. This means that in the present V₂O₅-rich glasses the presence of VO₅-tbp’s as found in crystalline Ca(VO₃)₂ cannot be completely ruled out only by the IR spectroscopy.

In short, the present IR study on the alkaline earth vanadates shows that major structural units in these glasses are VO₄-tetrahedra irrespective of the kind of alkaline earth metal and glass composition. Then, the VO₄-tetrahedra in the V₂O₅-rich compositions may be mainly present in the form of corner-sharing branched tetrahedral units as found in phosphate glasses. A more quantitative discussion on this subject will be made in the succeeding paper based on ⁵¹V NMR study.³⁷

5. Conclusion

The structure of alkaline earth vanadate glasses of the compositions xMgO·(100−x)V₂O₅ (x=30, 40), before and after hydration.

Taken to keep the glass samples out of moisture before and during the measurements. In the present magnesium vanadate glasses the occurrence of the absorption band at 1005 cm⁻¹ indicates that these glass samples have been already attacked by the moisture. Since all the samples were prepared in a similar manner, this means that the magnesium vanadate glasses are apt to be hydrated compared with other alkaline earth vanadate glasses. This tendency became more pronounced as the V₂O₅ content increased. This result may be explained as follows. Navabi et al.¹⁶ have shown that in amorphous V₂O₅ VO₄-tetrahedral units transformed into VO₅ units by hydration. If we assume that the vanadate glasses contain branched VO₄-tetrahedra as one of the constituent vanadate groups, the vanadate glasses may be attacked by ambient moisture. From this point of view, in magnesium vanadate glasses the contents of branched VO₄-tetrahedral units may be larger than in other alkaline earth vanadate glasses.

Fig. 5. IR spectra of magnesium vanadate glasses, xMgO·(100−x)V₂O₅ (x=30, 40), before and after hydration.

Acknowledgments This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan (No. 02403016).
References