The structure of alkaline earth vanadate glasses, \( x\text{MO} \cdot (100-x)\text{V}_2\text{O}_5 \) (\( M = \text{Ca}, \text{Sr}, \text{Ba} \), \( x = 30, 40, 45, 50, 55 \)), has been investigated by means of \( ^{51}\text{V} \) static and magic angle spinning (MAS) NMR spectroscopies. The \( ^{51}\text{V} \) NMR spectral parameters of various constituent vanadate groups contained in the vanadate glasses were determined by the spectrum simulation with reference to those of various crystalline vanadates obtained previously. It was found that the structure of alkaline earth vanadate glasses consists mainly of VO\(_4\) tetrahedra in accordance with the authors' previous results based on the IR study. It was deduced that for \( x = 50 \) the glass network is mainly constituted of one dimensional \((\text{VO}_3)_n\)-single chains, and for \( x \leq 45 \) the decrease of the MO content yields a mixture of the \( \text{V}_2\text{O}_5\)-rich phase constituted of three dimensionally branched VO\(_4\)-groups and the MO-rich phase constituted of the \( \text{VO}_5\)-trigonal bipyramids, followed by the decrease of \((\text{VO}_3)_n\)-single chains.

Key-words: Structure of alkaline earth vanadate glasses, \( ^{51}\text{V} \) static NMR, \( ^{51}\text{V} \) MAS NMR, VO\(_4\)-tetrahedra, \((\text{VO}_3)_n\)-single chains, Branched VO\(_4\)-groups, VO\(_5\)-trigonal bipyramids

2. Experimental

2.1 Sample preparation

Three series of alkaline earth vanadate glasses of the compositions, \( x\text{CaO} \cdot (100-x)\text{V}_2\text{O}_5 \) (\( x = 30, 40, 50 \), \( x\text{SrO} \cdot (100-x)\text{V}_2\text{O}_5 \) (\( x = 30, 40, 45, 50, 55 \)) and \( x\text{BaO} \cdot (100-x)\text{V}_2\text{O}_5 \) (\( x = 40, 45, 50 \), 55) were prepared using analytical-grade chemicals supplied by Nacalai Tesque, Kyoto. The procedures of preparation of these vanadate glasses have been described in our previous paper.\(^1\)

Crystalline alkaline earth vanadates, \( M_3(\text{VO}_4)_2 \), \( M_2\text{V}_2\text{O}_7 \), \( M(\text{VO}_3)_2 \) (\( M = \text{Ca}, \text{Sr}, \text{Ba} \)) were used as reference materials. The procedures of preparation of these crystalline vanadates have been described in our previous papers.\(^6,7\)

2.2 NMR measurements

\( ^{51}\text{V} \) static and MAS NMR spectra of powdered glass samples were recorded at 105 MHz (9.4 Tesla) on a JEOL JNM-GSX400 MAS FT-NMR spectrometer. A single pulse sequence was used; the pulse length of 0.5–1.0 μs corresponding to a pulse angle of \( \sim 22.5^\circ \), the pulse delay of 1 s and the accumulation of 1000 scans. A cylindrical zirconia sample holder was rotated at a speed of about 6 kHz during the \( ^{51}\text{V} \) MAS NMR measurements. The \( ^{51}\text{V} \) isotropic chemical shift, \( \delta_{iso} \), was measured with reference to crystalline \( \text{Zn}_3(\text{VO}_4)_2 \).

2.3 NMR spectra

The line broadening due to chemical shift...
anisotropy gives a typical powder pattern arising from an isotropic distribution of the direction of principal axes of the chemical shift tensor with respect to the external magnetic field.\(^8\) The theoretical spectrum can be obtained from the equations proposed by Bloembergen and Rowland.\(^9\) The principal components of the chemical shift tensors, \(\delta_1, \delta_2,\) and \(\delta_3\) are estimated by fitting the theoretical spectra to the static NMR spectra. The simulated spectra are obtained by convoluting a broadening function (Lorentz function) into the theoretical spectra, \(I(\delta)\), as follows;

\[
I(\delta') = \frac{1}{N} \int_{-\infty}^{\infty} \frac{I(\delta)}{H_0 + (\delta' - \delta)^2} d\delta
\]

where \(I(\delta')\) is broadened powder pattern giving the simulated spectrum, \(N\) the normalization factor and \(H_0\) the line width.

The chemical shift anisotropy, \(\Delta \delta\), and the asymmetry parameter, \(\eta\), can be determined using the following definitions:\(^{10}\)

\[
\Delta \delta = \delta_3 - \frac{\delta_1 + \delta_2}{2}
\]

\[
\eta = \frac{\delta_2 - \delta_1}{\delta_3 - \delta_{iso(stat)}}
\]

\[
\delta_{iso(stat)} = \frac{\delta_1 + \delta_2 + \delta_3}{3}
\]

where \(\delta_{iso(stat)}\) is the isotropic chemical shift and \(\delta_1, \delta_2,\) and \(\delta_3\) the principal component of chemical shift tensors. The principal component of the chemical shift tensors can be determined based on Eq. (5).

\[
|\delta_3 - \delta_{iso(stat)}| \geq |\delta_1 - \delta_{iso(stat)}| \geq |\delta_2 - \delta_{iso(stat)}|
\]

3. Results

Figure 1(a), (b) and (c) show the \(^{51}\)V static and MAS NMR spectra of \(x\text{CaO} \cdot (100 - x) \text{V}_2\text{O}_5\) \((x=30, 40, 50), x\text{SrO} \cdot (100 - x) \text{V}_2\text{O}_5\) \((x=30, 40, 45, 50, 55)\) and \(x\text{BaO} \cdot (100 - x) \text{V}_2\text{O}_5\) \((x=40, 45, 50)\) glasses, respectively. The peak positions of the \(^{51}\)V MAS NMR spectra are almost the same as those of the corresponding \(^{51}\)V static NMR spectra. For \(x \geq 50\), these static NMR spectra consist of only one peak and their peak positions are almost invariant at \(-62\) to \(-66\) ppm independent of the kinds of the \(\text{M}^{2+}\) cations. For \(x \leq 45\), these static NMR spectra of \(x\text{MO} \cdot (100 - x) \text{V}_2\text{O}_5\) \((\text{M}=\text{Ca}, \text{Sr}, \text{Ba})\) glasses have a shoulder at a high frequency of ca. 220 ppm and a long tail extending up to low frequencies. Since the peak positions of the \(^{51}\)V MAS NMR spectra were found independent of the sample spinning speed ranging from 5 to 6 kHz and the several spinning side bands (SSB's) were observed for \(55\text{SrO} \cdot 45\text{V}_2\text{O}_5, 50\text{SrO} \cdot 50\text{V}_2\text{O}_5, 50\text{BaO} \cdot 50\text{V}_2\text{O}_5\) glasses as denoted by the asterisks in the figures, these peak positions are taken as the \(^{51}\)V isotropic chemical shifts, \(\delta_{iso}\), of these vanadate glasses.

The variation of the line profiles with the \(\text{MO}\) content may be well represented by the differential spectra. Figure 2 (a), (b) and (c) show the differential spectra of the \(^{51}\)V static NMR spectra of \(x\text{CaO} \cdot (100 - x) \text{V}_2\text{O}_5\), \(x\text{SrO} \cdot (100 - x) \text{V}_2\text{O}_5\) and \(x\text{BaO} \cdot (100 - x) \text{V}_2\text{O}_5\) glasses, respectively. For example, the line profiles of differential spectra of (B)-(A) in Fig. 2 (a), (C)-(B) in Fig. 2 (b) and (B)-(A) in Fig. 2 (c) are very similar to each other in both peak position and shape. It should be, however, noted that in the differential spectral profiles other broad peaks appear on the both sides of the main peak when the

![Fig. 1. \(^{51}\)V static and MAS NMR spectra of alkaline earth vanadate glasses. (a) \(x\text{CaO} \cdot (100 - x) \text{V}_2\text{O}_5\) \((x=30, 40, 50)\), (b) \(x\text{SrO} \cdot (100 - x) \text{V}_2\text{O}_5\) \((x=30, 40, 45, 50, 55)\), (c) \(x\text{BaO} \cdot (100 - x) \text{V}_2\text{O}_5\) \((x=40, 45, 50)\). The MAS NMR peak positions are indicated by the numerical value.](image-url)
4. Discussion

4.1 $^{51}$V chemical shift

We have recently found\(^{6),7}\) that many crystalline vanadates having crystallographically inequivalent vanadium sites exhibit the same number of $^{51}$V isotropic chemical shifts, $\delta_{iso}$'s as the sites, which were determined from the position of a main peak independent of the sample spinning speed. In such case it was easy to differentiate the main peak from spinning side bands (SSB's) because the line broadening of main peak was ca. 20 ppm, which was small compared with the SSB intervals of ca. 60 ppm at a spinning rate of 6 kHz. As is evident from Fig. 2, however, in the present vanadate glasses only a broad peak occurred and SSB's at intervals of ca. 60 ppm were obscured, indicating that a number of $\delta_{iso}$'s may exist, that is, the line broadening due to site distribution is larger than the SSB intervals of ca. 60 ppm.

In crystalline vanadates the average $\delta_{iso}$'s of $^{51}$V were found to decrease with decreasing electronegativity of the second neighboring cations, M\(^{2+}\).\(^{6),7}\)

In Fig. 3 the $\delta_{iso}$'s of alkaline earth vanadate glasses are plotted against Pauling’s electronegativity (EN) of the alkaline earth metal atom together with the previous data of the crystalline alkaline earth vanadates.\(^{5),7}\) For each series of glasses, no significant dependence of the $\delta_{iso}$'s on the electronegativity is seen. It is interesting to note that the $\delta_{iso}$'s of alkaline earth vanadate glasses are very similar to the $^{51}$V isotropic chemical shifts of corresponding crystalline alkaline earth pyrovanadates rather than crystalline metavanadates. The fact may indicate that all these vanadate glasses contain $V_2O_7^{4-}$

4.2 Chemical shift anisotropy

The chemical shift anisotropy, $|\Delta \delta|$, which describes the orientation dependence of the three dimensional shielding of a nucleus against the external magnetic field, should be related to the asymmetrical distribution of electron density around the nucleus, which in turn reflects the local environment of an atom of interest. We have found in the previous studies\(^{6),7}\) that for various crystalline vanadates the chemical shift anisotropy, $|\Delta \delta|$, is closely correlated with both the coordination number of a vanadium atom and the polymerization degree. That is, $|\Delta \delta|$ is larger in the VO\(_5\)-trigonal bipyramids than in
the VO₄-tetrahedral unit and for the same VO₄-tetra-
hedra it increases in the order, ortho-< pyro-
<metavanadates, as the polymerization degree in-
creases.

Figure 4 compares the ⁵¹V static NMR spectra of
the alkaline earth metavanadate glasses with those
of the crystalline alkaline earth pyrovanadates mea-
sured previously⁶ since their ⁵¹V isotropic chemical
shifts determined from the ⁵¹V MAS NMR spectra
agreed with each other as noted in previous section.
Nevertheless, the ⁵¹V static NMR line shapes of alka-
ine earth metavanadate glasses, which are asym-
metrical and broad, do not resemble those of crystal-
line alkaline earth pyrovanadates. In view of the
glass composition, it is not reasonable to consider
that the glass networks are constituted of V₂O₇⁴⁻
groups only. Accordingly, those glasses should con-
tain other types of vanadate groups in addition to
pyrovanadate groups. It should be noted that the ⁵¹V
static NMR spectra of xMO·(100−x)V₂O₅ (M=Ca,
Sr, Ba, x≤45) glasses are characterized by a shoul-
der or peak at 220–250 ppm, assigned to an axial
component, δ₁ (=δ₂) of V₂O₅ crystal.⁷

It is assumed that the differential spectra between
two glasses with different compositions provide an in-
formation on the compositional changes in con-
stituent group. Figure 5 shows the ⁵¹V static NMR
spectra and differential spectra of the xSrO·
(100−x)V₂O₅ (x=30, 40, 45, 50, 55) glasses, and
their simulated spectra. For example, the (B)−(A)
differential spectrum represents the second con-
stituent group present in 50SrO·50V₂O₅ glass, and
can be simulated by one peak (Peak 2), whose spec-
tral parameters such as chemical shift tensors, full

width at the half maximum (FWHM) of Lorentz
function, chemical shift anisotropy, Aδ, and asym-
metry parameter, η, are listed in Table 1. Similarly,
the (A)−(B) differential spectrum can be simulated
by one peak (Peak 1), whose spectral parameters
are also listed in Table 1. It is significant to note that
the spectral parameters of Peak 1 are compatible
with those of pyrovanadate groups, indicating that
the Peak 1 is attributable to V₂O₇⁴⁻ groups.
Moreover, taking into the fact that V₂O₇⁴⁻ groups
are contained in alkaline earth vanadate glasses as
judged from the δiso values, the ⁵¹V static NMR spec-
tra of 50SrO·50V₂O₅ and 55SrO·45V₂O₅ glasses can
be convoluted by two kinds of peaks, Peak 1
(pyrovanadate group) and Peak 2, whose spectral
parameters are listed in Table 1. Since the spectral
profiles of 50MO·50V₂O₅ glasses (M=Ca, Sr, Ba)
are very similar to each other, the same procedure
can be applied to other 50MO·50V₂O₅ glasses (M=
Ca, Ba). The obtained spectral parameters are also
listed in Table 1.

The (C)−(B) differential spectrum in Fig. 5 can
be convoluted by at least two kinds of peaks, Peak 2
and Peak 4, indicating the presence of another vana-
date group. Then both the (D)−(B) and the (E)−
(B) differential spectra can be convoluted by at
least two kinds of peaks, Peak 3 and Peak 4, both
which are not present in 50SrO·50V₂O₅ glass. This
is also the case for other differential spectra in Figs.
2(b) and (c). Accordingly, the ⁵¹V static NMR spec-
tra of xMO·(100−x)V₂O₅ glasses (x≤45) can be
convoluted by four kinds of peaks such as Peak 1,
Peak 2, Peak 3 and Peak 4. The obtained spectral
parameters of respective peaks are also listed in Ta-
ble 1.

Fig. 4. ⁵¹V static NMR of alkaline earth metavanadate glasses and crystalline alkaline earth pyrovanadates.
Fig. 5. Simulated and experimental spectra of xSrO·(100−x)V₂O₅ (x=30, 40, 45, 50, 55) glasses.
Fig. 6. Plots of the asymmetry parameter, η, vs. the chemical shift anisotropy, |Aδ|, for alkaline earth vanadate glasses and various crys-
talline vanadates.⁶,⁷
Table 1. Chemical Shift Parameters Used in the Simulated Spectra, Chemical Shift Anisotropy and Asymmetry Parameter

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak 1</th>
<th>Peak 2</th>
<th>Peak 3</th>
<th>Peak 4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>δ&lt;sub&gt;1&lt;/sub&gt;</td>
<td>δ&lt;sub&gt;2&lt;/sub&gt;</td>
<td>δ&lt;sub&gt;3&lt;/sub&gt;</td>
<td>δ&lt;sub&gt;4&lt;/sub&gt;</td>
</tr>
<tr>
<td>50CatO:50V&lt;sup&gt;2&lt;/sup&gt;O&lt;sub&gt;5&lt;/sub&gt;*</td>
<td>0 -50-130</td>
<td>70 -60-105</td>
<td>0.71 21</td>
<td>30 -50-300</td>
</tr>
<tr>
<td>50CatO:50V&lt;sup&gt;2&lt;/sup&gt;O&lt;sub&gt;5&lt;/sub&gt;*</td>
<td>0 -50-130</td>
<td>70 -60-105</td>
<td>0.71 20</td>
<td>30 -50-300</td>
</tr>
<tr>
<td>50CatO:50V&lt;sup&gt;2&lt;/sup&gt;O&lt;sub&gt;5&lt;/sub&gt;*</td>
<td>5 -25-125</td>
<td>90 -46-115</td>
<td>0.39 18</td>
<td>50 -10-100</td>
</tr>
<tr>
<td>50CatO:50V&lt;sup&gt;2&lt;/sup&gt;O&lt;sub&gt;5&lt;/sub&gt;*</td>
<td>0.5 -25-125</td>
<td>90 -46-115</td>
<td>0.39 20</td>
<td>50 -10-100</td>
</tr>
<tr>
<td>Sr(SO&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>- - - - -</td>
<td>- - - - -</td>
<td>- - - - -</td>
<td>- - - - -</td>
</tr>
<tr>
<td>Sr&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>- - - - -</td>
<td>- - - - -</td>
<td>- - - - -</td>
<td>- - - - -</td>
</tr>
<tr>
<td>Ba&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>- - - - -</td>
<td>- - - - -</td>
<td>- - - - -</td>
<td>- - - - -</td>
</tr>
<tr>
<td>Ca&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>- - - - -</td>
<td>- - - - -</td>
<td>- - - - -</td>
<td>- - - - -</td>
</tr>
</tbody>
</table>

All the values except η and area have a unit of ppm. Asterisks denote glasses. Others are crystalline substances.

For comparison, the data of corresponding crystalline alkaline earth vanadates are also shown. It should be pointed out from Table 1 that the FWHM’s of respective peaks are fairly large compared with those in crystalline vanadates (ca. 20 ppm) and the SSB intervals of ca. 60 ppm, while their δ<sub>iso</sub> values are very close to each other. This experimental fact clearly shows that the structural units of a vanadate group have a broader site distribution in glass than in corresponding crystals.

In Fig. 6 the asymmetry parameter, η, is plotted against the chemical shift anisotropy, |δ<sub>iso</sub>|, not only for alkaline earth vanadate glasses but also for various crystalline vanadates previously studied. For a better understanding, the areas, where the same vanadate groups in vanadate crystals are present, are shown in the figure. Figure 6 indicates that for x ≥ 0.45 the two NMR parameters, η and |δ<sub>iso</sub>|, of Peak 2 are almost identical to those in corresponding metavanadate crystals. Irrespective of the kind of alkaline earth metal, these parameters fall in the “intermediate” region, to which crystalline Sr(V<sub>2</sub>O<sub>5</sub>)<sub>2</sub> and Ba(V<sub>2</sub>O<sub>5</sub>)<sub>2</sub> consisting of VO<sub>4</sub>-tetrahedra with relatively large V═O bond length of ~1.8Å belong. This means that the metavanadate group of (VO<sub>3</sub>)<sub>n</sub> single chain contained in these metavanadate glasses bears a marked structural resemblance to those in crystalline Ba(V<sub>2</sub>O<sub>5</sub>)<sub>2</sub> in excellent agreement with the previous IR study. Accordingly, the local structure of metavanadate glasses is mainly characterized by two kinds of vanadate groups such as V<sub>2</sub>O<sub>7</sub><sup>4-</sup> (Peak 1) and intermediate group constituted of (VO<sub>3</sub>)<sub>n</sub>-single chain (Peak 2).

For x ≤ 0.45 the area of Peak 3 is different from that of intermediate group because the chemical shift anisotropy, |δ<sub>iso</sub>|, of Peak 3 is slightly larger but the asymmetry parameter, η, is much smaller than that of intermediate group, indicating that the coordination state around a vanadium atom and/or the polymerization state of VO<sub>3</sub>-polyhedra yielding Peak 3 may be somewhat different from the (VO<sub>3</sub>)<sub>n</sub>-single chain (Peak 2). Although the location of Peak 4 is different in terms of the asymmetry parameter from that of (VO<sub>3</sub>)<sub>n</sub>-zigzag chain group, the η value of Peak 4 is larger than that of V<sub>2</sub>O<sub>5</sub> crystal and is very close to that of Ca(V<sub>2</sub>O<sub>5</sub>)<sub>2</sub> crystal. This may indicate that the V═O double bond character of the vanadate group corresponding to Peak 4 is weak compared with that of (VO<sub>3</sub>)<sub>n</sub>-zigzag chain group. Accordingly, it is considered that the local structure of xMO<sub>1</sub>E(100-x)V<sub>2</sub>O<sub>5</sub> glasses containing less than 45 mol% MO is characterized by at least four kinds of vanadate groups such as V<sub>2</sub>O<sub>7</sub><sup>4-</sup> (Peak 1), (VO<sub>3</sub>)<sub>n</sub>-single chains (Peak 2), (VO<sub>3</sub>)<sub>n</sub>-zigzag chains constituted of VO<sub>3</sub>-trigonal bipyramids as found in Ca(V<sub>2</sub>O<sub>5</sub>)<sub>2</sub> crystal and probably condensed VO<sub>4</sub>-tetrahedral group (Peak 3) which is different from the (VO<sub>3</sub>)<sub>n</sub>-single chain found in crystalline Ba(V<sub>2</sub>O<sub>5</sub>)<sub>2</sub>. The nature of Peak 3 will be mentioned in the following section.
4.3 Compositional dependence of the structure of alkaline earth vanadate glasses

Since the NMR peak area is assumed to be proportional to the abundance of a nucleus, the percentage of each vanadate group can be estimated from the ratio of respective peak areas deconvoluted in a manner as shown in Fig. 5. The result is shown in Table 1. The reliability factor,

\[
R_t = \frac{\sum |I_{obs} - I_{calc}|}{\sum |I_{obs}|},
\]

in the present peak convolution was within 7-12%. Figure 7 shows the compositional dependence of the percentage of each peak area in \(x\text{MO} \cdot (100-x)\text{V}_2\text{O}_5\) glasses. No significant effects of the kind of \(M^{2+}\) on the compositional dependence of the peak area are seen. This again implies that the glass networks of these alkaline earth vanadate glasses are similar to each other. A large portion of the peak area is contributed by Peaks 2 and 3 at any compositions, indicating that most of the glass networks are composed of \(\text{VO}_4\)-tetrahedra. This result is in agreement with the results obtained from IR spectra.\(^1\) The peak area of Peak 4 decreases with increasing MO content, indicating that the fraction of \((\text{V}_2\text{O}_8)_n\)-chain in the vanadate glass network decreases with increasing MO content. This result is in agreement with the conclusion by Dimitriev and Dimitrov\(^4\) that the introduction of alkaline earth metal oxide into \(\text{V}_2\text{O}_5\) matrix causes a change in structural unit from \(\text{VO}_5\)-groups to \(\text{VO}_4\)-groups.

For silicate melts and glasses the \(\text{SiO}_4\)-tetrahedra are classified by \(Q^n\) (\(n=0-4\)) depending on the number of bridging oxygens. The changes in \(Q^n\) species in a silicate glass with composition are described by the following equation,\(^5\)

\[
2Q^n \rightarrow Q^{n+1} + Q^{n-1}
\]

Similarly, if we assume that alkaline earth metavanadate glasses, \(50\text{MO} \cdot 50\text{V}_2\text{O}_5\) (\(M=\text{Ca}, \text{Sr}, \text{Ba}\)), are composed of various vanadate anions present in the vanadate crystals, the contents of respective vanadate groups in glasses can be determined by the following equilibrium equation at melting temperature,

\[
2\text{M(VO}_3)_2 = \text{M}_2\text{V}_2\text{O}_7 + \text{V}_2\text{O}_5
\]

According to Eq. (7) the percentage of \(\text{V}_2\text{O}_7^{4-}\) group and \((\text{V}_2\text{O}_8)_n\)-chain must be equal. It is understood that the increase of alkaline earth metal oxide content up to 55 mol\% results in the production of \(\text{V}_2\text{O}_7^{4-}\)-groups. Moreover, the existence of \(\text{V}_2\text{O}_7^{4-}\)-groups in the composition, \(50\text{MO} \cdot 50\text{V}_2\text{O}_5\) (\(M=\text{Ca}, \text{Sr}, \text{Ba}\)) can be explained by assuming the above equilibrium reaction. However, on the basis of the results obtained by IR\(^1\) and NMR there is no evidence for the presence of \(\text{VO}_3\)-trigonal bipyramids as found in crystalline \(\text{V}_2\text{O}_5\). This indicates that the equilibrium expressed by Eq. (7) lies to the left for alkaline earth metavanadate glasses. An X-ray RDF analysis performed by Morikawa et al.\(^15\) has shown that the structure of molten \(\text{V}_2\text{O}_5\) is similar to the crystal structure of \(\text{P}_2\text{O}_5\) or disilicates, in which each tetrahedron is surrounded by three tetrahedra (branched \(\text{VO}_4\)-group). Considering that the glass network structure reflects the structure of a melt at high temperatures, vanadate glasses also have a \(\text{P}_2\text{O}_5\)-like structure composed of \(\text{VO}_4\)-tetrahedra. Consequently, the alkaline earth vanadate glasses of \(\text{V}_2\text{O}_5\)-rich phase, in which the excess charge can not be compensated by alkaline earth metal cations, are composed of not only \((\text{V}_2\text{O}_8)_n\)-chains found in \(\text{Ca}(\text{VO}_3)_2\)\(^11\)) and \(\text{V}_2\text{O}_5\)\(^12\)) crystal but also branched \(\text{VO}_4\)-groups.

A \(^{31}\text{P}\) NMR measurement performed by Duncan and Douglass\(^16\) showed that the chemical shift anisotropy increases with the polymerization degree of \(\text{PO}_4\)-tetrahedra in the order, end group < \((\text{PO}_3)_n\)-group < \(\text{PO}_3\)-ring group < branched \(\text{PO}_4\)-group. This relation may hold for the present case. It is therefore possible to predict the polymerization degree of the vanadate anions on the basis of the following increasing order of chemical shift anisotropy, \(|\Delta\delta|, \text{VO}_3^- (\leq 77 \text{ ppm}) < \text{V}_2\text{O}_7^{4-} (93-177 \text{ ppm}) < \text{V}_2\text{O}_7^{4-}\)-single chain \((\geq 254 \text{ ppm}) < \text{V}_2\text{O}_7^{4-}\)-zigzag chain \((\geq 476 \text{ ppm})\). According to this order, Peak 3 can be assigned to the branched \(\text{VO}_4\)-group, because the \(|\Delta\delta|\) value ranges from 430 to 448 ppm as seen from Table 1.

On decreasing MO content down to 30 mol\% the branched \(\text{VO}_4\)-groups become dominant and any pyrovanadate groups should not coexist in these
vanadate glasses. Nevertheless, the presence of \( V_2O_4^{4-}\)-groups in low MO-containing vanadate glasses was recognized. Such unexpected behavior can be explained by considering that VO\(_4\)-end groups of \( (VO_3)\_n\)-single chains \( O_3V-O-(VO_3)\_n \) or branched VO\(_4\)-groups \( O_3V-(VO_4)\_n \) having three non-bridging oxygens present in these vanadate glasses exhibit the same NMR signal as \( V_2O_7^{4-}\)-group. That is, this means that the \( (VO_3)\_n\)-single chains or branched VO\(_4\)-groups are not very large in size. In addition, on the basis of the results obtained by IR\(^1\) even in the \( V_2O_5\)-rich glasses, there is no evidence for the presence of VO\(_5\)-trigonal bipyramids as found in crystalline \( V_2O_5\). As a result of our IR study\(^1\) and the present NMR study, the change in vanadate groups in alkaline earth vanadate glasses with compositions can be described by the following equations,\(^8\)

\[
2M(VO_3)_2{(VO_3)\_n\text{-single chains}} = (V_2O_8)\_n\text{-zigzag chains} \\
\Rightarrow M_2V_2O_7{(V_2O_7)^{4-}\text{-groups}} + V_2O_5{(\text{branched VO}_4\text{-groups})}
\]

In Fig. 8 the structure model of alkaline earth vanadate glasses of about 40 mol% MO is proposed on the basis of the present results.

5. Conclusion

The structure of alkaline earth vanadate glasses, \( xMO\cdot(100-x)V_2O_5\) (M = Ca, Sr, Ba; \( x = 30, 40, 45, 50, 55 \)) has been investigated by means of \( ^{51}\text{V} \) static and MAS NMR spectroscopies. The following conclusions were drawn.

1. The structure of these alkaline earth vanadate glasses basically consists of VO\(_4\)-tetrahedra.
2. For \( x \geq 50 \), the increase of MO (M = Ca, Sr, Ba) content causes the formation of \( V_2O_7^{4-}\)-groups.
3. For \( x = 50 \) the glass network is mainly constituted of one dimensional \( (VO_3)\_n\)-single chains.
4. For \( x \leq 45 \), the decrease of the MO content causes the formation of \( V_2O_5\)-rich phase having three dimensional arrangements of branched VO\(_4\)-groups. On the other hand, the MO-rich groups, M(VO\(_3\))\(_2\) may be composed of \( (V_2O_8)\_n\)-zigzag chains found in Ca(VO\(_3\))\(_2\) crystal. The fractions of these vanadate groups follow the equilibrium reaction,

\[ (VO_3)\_n\text{-single chains} \Leftrightarrow (V_2O_8)\_n\text{-zigzag chains} \]

depending on the MO content.

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References


Fig. 8. The proposed structural model of alkaline earth vanadate glasses. Small closed circles represent vanadium atoms, small open circles oxygen atoms and large open circles alkaline earth metal atoms.