Studies on Constitution of Vitreous Silicate by Infrared Absorption Spectra

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The infrared absorption studies have been carried out on the silicate glasses as an approach to clarify the constitution of molten silicate. As seen in the figures of infrared absorption spectra obtained for the binary silicates of PbO-SiO₂, CaO-SiO₂, BaO-SiO₂, ZnO-SiO₂ and Na₂O-SiO₂ systems, each vitreous silicate gives characteristic spectral curves. From the result of investigation on the absorption band of ν_3 vibration due to Si-O stretching mode, it may be predicted that the different kinds of silicate anion can co-exist in vitreous or molten silicates over a certain SiO₂ content.

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I. Introduction

The constitution of molten silicate or slags has been investigated by measuring the structure sensitive properties such as density, viscosity, surface tension or electrical conductivity. Since it is considered that the structure of silicate or slag melts is preserved in vitreous silicate at room temperature, the results obtained for molten silicate can be applied to the studies on silicate glasses and those obtained in vitreous silicate by X-ray analysis or the infrared absorption technique will be applicable to the field of liquid silicate. As for a model of silicate glasses, Mackenzie⁽¹⁾ summarized the various pictures so far presented and established his own view based on discrete anion theory.

The infrared absorption spectra of silicate crystal or glass has been measured and demonstrated as one of the direct methods for obtaining a structural picture. Saksena⁽²⁾ carried out extensive work on infrared absorption spectra of various types of silicate minerals and compared those experimental results with calculated values. Miller et al.⁽³⁾ and McDevitt et al.⁽⁴⁾ summarized the infrared absorption studies on inorganic compounds. Simon et al.⁽⁵⁾, Florinskaya et al.⁽⁶⁾, Cherneva et al.⁽⁷⁾ and Tarte⁽⁸⁾ presented the papers concerning glassy or crystalline silicates. Although more data should be needed in order to assign each absorption band to the vibrational mode and in silicate glasses and other amorphous or noncrystalline substances, only broad absorption bands are observed on infrared spectral curves due to the spread of force constant of the bonds in glass lattice, the measurements of a shift of absorption band due to the changing of SiO₂ content or the comparison of the bands with those of other silicates will be of great importance for a structural approach to the silicate melts or glasses. As seen in binary phase diagrams of metal oxide and silica, it is obvious that the effect of metal

oxide on silicate anion will be quite different even though the same amount of metal oxide is introduced. For instance, in the PbO-SiO₂ system, there exist one continuous liquid phase and three stable compounds. On the other hand, in the ZnO-SiO₂ system, two wide liquid ranges appear on the SiO₂ side and its stable compound is only one as 2ZnO·SiO₂. It can be said, therefore, that the characteristic silicate model of each metal oxide-silica system should be presented rather than a generalized picture. In this paper, the vitreous samples in PbO-SiO₂, ZnO-SiO₂, BaO-SiO₂, Na₂O-SiO₂ and CaO-SiO₂ systems were chosen for infrared absorption studies.

II. Experimental Procedure

The SiO₂ used was pure quartz (rock crystal) powder and other metal oxides were analytical grade reagents. Na₂O and CaO were introduced as carbonates. Metallic oxide and silica were mixed and melted in a Pt crucible (below 1600°C) or a Pt crucible containing 30% Rh (above 1600°C). The vitreous samples were obtained by rapid cooling from a temperature above the melting point of the silicates after keeping for 1~3 hr and stirring in a complete molten state. In the case of PbO-SiO₂ and ZnO-SiO₂ systems molten silicate can be poured into water, while CaO-SiO₂, Na₂O-SiO₂ and BaO-SiO₂ systems, which react with water, are cooled with water from outside of the crucible. About 100 mg of the samples which are apt to crystallize while cooling are weighed and subjected to quenching into mercury after melting in the Pt envelope containing 30% Rh. The samples obtained are ground to the diameter of less than 2 μ with an alumina mortar. For the Na₂O-SiO₂ system, grinding and mixing should be carried out in benzene or argon gas atmosphere in order to prevent from reacting with H₂O or CO₂. About 0.5~1.5 mg of the vitreous samples were mixed with 200 mg of KBr powder in alumina mortar and pressed into a

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pellet under 10t/cm² in vacuum. The infrared absorption spectra were obtained with the Shimadzu IR-600 or IR-27G spectro-photometer equipped with grating, covering the range of 1700~400cm⁻¹.

III. Experimental Results

1. Na₂O-SiO₂ system

The spectral curves obtained in the Na₂O-SiO₂ system are shown in Fig. 1. The strong absorption band in the 1100~900cm⁻¹ region is ascribed to Si-O stretching vibrations (ν_3). The absorption bands around 800cm⁻¹ and 470cm⁻¹ are assigned as stretching mode (ν_1) and Si-O-Si bending mode (ν_4) respectively. In this paper, the change of absorption band due to stretching vibration (ν_3) with metal oxide contents will mainly be discussed. In vitreous silica the absorption peak of ν_3 vibration, which is observed at about 1110cm⁻¹, tends to shift to a lower frequency, 1065cm⁻¹ at 80% SiO₂*, as Na₂O is added, due to a decrease of the number of bridging oxygen in silicate anion. Further addition of Na₂O resulted in the appearance of a new absorption peak, which continuously shifts to 930cm⁻¹ for 60% SiO₂ with increasing Na₂O content. Beyond this composition, as seen in Fig. 1, the absorption band of 1065cm⁻¹ again shifts toward a lower wave number, finally about 990cm⁻¹ for 40% SiO₂, as Na₂O is increased.

Fig. 1 Infrared absorption spectra of sodium silicate glasses.

2. CaO-SiO₂ system

The absorption spectra in this system are shown in Fig. 2. The absorption peak at 1110cm⁻¹ observed in pure vitreous silica shifts to 1100cm⁻¹ by 10% addition of CaO, which remains unchanged until 65% SiO₂. On the other hand, another peak around 930cm⁻¹ appears for 72% SiO₂ and remains until 55% SiO₂, getting intenser as the CaO content is increased. Between them one more absorption band exists, that is, about 1065cm⁻¹

at 70% SiO₂, 1030cm⁻¹ at 60~55% SiO₂, and 1010cm⁻¹ at 50% SiO₂. The absorption band of 965cm⁻¹ is observed at the compositions of 45~40% SiO₂. The samples containing 35% SiO₂ seemed to partly crystallize during cooling, showing characteristic sharp absorption bands in the curve.

3. BaO-SiO₂ system

As seen in Fig. 3, the absorption maxima of ν_3 stretching vibration shifts toward the lower wave number

Fig. 2 Infrared absorption spectra of calcium silicate glasses.

Fig. 3 Infrared absorption spectra of barium silicate glasses.

* SiO₂ content in binary silicate is expressed in mole% unless otherwise mentioned.

side, i.e., from 1110cm^{-1} in pure SiO_2 to 1020cm^{-1} for 70% SiO_2 as the amount of BaO is increased. Then new absorption peak in the $920\sim 930\text{cm}^{-1}$ region appears and becomes intenser with increasing BaO, while the absorption peak of 1020cm^{-1} still remains. For the silicates containing less than 45% SiO_2 , however, the absorption peak of 1020cm^{-1} seemed to shift to a lower wave number.

Fig. 4 Infrared absorption spectra of zinc silicate glasses.

Fig. 5 Infrared absorption spectra of lead silicate glasses.

4. ZnO-SiO_2

The results on this system are shown in Fig. 4. The characteristic figure in this system is that no continuous shift of the absorption bands was observed over the whole experimental range. On the addition of ZnO to silica, it should be noted that the intensity in absorption of 1110cm^{-1} becomes weaker and another band at 930cm^{-1} becomes stronger. In the regions with less band than 40% SiO_2 , absorption band of 1110cm^{-1} disappeared and only the band of 930cm^{-1} remains.

5. PbO-SiO_2 system

The spectral curves obtained for the PbO-SiO_2 system are shown in Fig. 5. The absorption maxima due to Si-O stretching vibration shift continuously to a lower wave number, 890cm^{-1} at 30% SiO_2 , as the melt becomes richer in PbO, and then the absorption peak remains constant even with further addition of PbO.

IV. Discussion

Summarized spectral data of vitreous samples in the above-mentioned binary silicates are shown in Fig. 6. In the PbO-SiO_2 system, as seen clearly in this figure, the wave number of the absorption peak decreases almost linearly with increasing PbO content in the silicate. In the ZnO-SiO_2 system, the immiscibility in the liquid phase is observed on the silica rich side, i.e., more than about 65% SiO_2 . The absorption spectra of the samples on the silica side are similar to pure vitreous silica, and those on the ZnO side are similar to that of 60% SiO_2 . The spectral data are quite contrary to those of the PbO-SiO_2 system and only two absorption bands are observed. The BaO-SiO_2 system exhibits a S-shaped solidification curve on the phase diagram. As BaO is added to silica, the absorption band at first continuously shifts to a lower wave number until at 65% SiO_2 , and then splits into

Fig. 6 Relation between wave number of absorption peak (ν_3) and SiO_2 content in binary silicate glasses.

two peaks which remain almost unchanged even with further addition of BaO. The CaO-SiO₂ system shows liquid immiscibility for more than about 70% SiO₂. The absorption bands around 1100cm⁻¹ and 930cm⁻¹ are observed as in the ZnO-SiO₂ system. In addition, one more absorption band is seen, shifting with the change in composition. In the Na₂O-SiO₂ system, as mentioned before, the absorption band at first gradually shifts up to 1065cm⁻¹ with the addition of Na₂O and splits into two peaks.

If the wave number of the absorption bands in Fig. 6 which stay constant independent of the change in composition are taken into account, six kinds of absorption bands are observed on the curves. If it is assumed that such absorption peaks are attributed to the difference of silicate anions in each silicate, the following six silicate anions will be considered as constituents.

1. Absorption peak around 900 cm⁻¹

Saksena pointed out that the absorption band due to the ν_3 vibration of SiO₄⁴⁻ is located at 893cm⁻¹. In the PbO-SiO₂ system, as seen from the results obtained, one strong absorption peak due to the ν_3 vibration of silicate anion was shown on the spectral curves over the whole experimental range. The silicates containing less than 33.3% SiO₂ may be considered to have SiO₄⁴⁻ (as silicate anion) and the absorption peaks for the composition are located around 900~890cm⁻¹. This absorption peak, therefore, may be assigned to the ν_3 vibration of SiO₄⁴⁻.

2. Absorption peak around 930 cm⁻¹

In the PbO-SiO₂ system, the composition having this absorption peak corresponds to 40% SiO₂, i.e., Si₂O₇²⁻ as silicate anion. During crystallization of vitreous lead silicate containing 40% SiO₂, it was found that the unstable compound Pb₃(Si₂O₇) once formed and then dissociated into PbSiO₃ and Pb₂SiO₄ for further heat treatment⁽⁹⁾. In the ZnO-SiO₂ system, there exists no compound like 3ZnO·2SiO₂ on the equilibrium phase diagram. On crystallization of glassy zinc silicate, however, the unstable compound whose structure is just the same as de-hydrated crystal of calamine [Zn₄(Si₂O₇)(OH)₂·2H₂O] on the X-ray pattern is formed before changing into stable Zn₂SiO₄. Consequently, in the silicate melt or glass, there may be silicate anion Si₂O₇²⁻ which will be assigned to 930cm⁻¹ as the absorption band.

3. Absorption peak around 970 cm⁻¹

Since the absorption band of PbO-SiO₂ (50% SiO₂) corresponds to 970cm⁻¹ as shown in the PbO-SiO₂ system, this peak may be assigned to Si_nO_{3n}²ⁿ⁻ ($n \geq 3$) as a ring structure of silicate anion.

4. Absorption peak around 1020 cm⁻¹

In the PbO-SiO₂ system, the absorption peak of the composition having 66% SiO₂ appears at 1020cm⁻¹, which is also found in the absorption of BaSi₂O₅ in the BaO-SiO₂ system. Hence this peak will be attributed to the ν_3 vibration in the Si_{2n}O_{5n}²ⁿ⁻ ($n \geq 3$) layer structure or discrete anion.

5 Absorption peak around 1065 cm⁻¹

This absorption peak corresponds to that of the compound MO·4SiO₂ in BaO-SiO₂, Na₂O-SiO₂ systems. Silicate anion will be shown as three dimensional complex ions like Si₁₂O₂₇⁶⁻ or Si₁₆O₃₆⁸⁻.

6. Absorption peak around 1100 cm⁻¹

This peak is attributed to the ν_3 vibration of vitreous silica. As a result of the above consideration, it may be said that two or three different kinds of silicate anions could co-exist in such silicate melts as ZnO-SiO₂, BaO-SiO₂, CaO-SiO₂ and Na₂O-SiO₂ systems. In the PbO-SiO₂ system, the silicate network will continuously break down into smaller structural units as PbO is added to SiO₂, and the resulting infrared absorption band also shifts continuously from a higher wave number to the lower one. Since no change in silicate anion will be expected for the silicates containing less than 33% SiO₂, the absorption band will remain constant. In the ZnO-SiO₂ system, the addition of ZnO to the silica network causes a rupture of Si-O bonds and results in the formation of Si₂O₇²⁻ type ion. None of other type of silicate anion will exist in the silicate melts for the compositional range examined. Since zinc silicates less than 30% SiO₂ were impossible to obtain in a glassy state, it is not clear if they have other types of ion like SiO₄⁴⁻. When BaO is added to SiO₂, the silicate network gradually breaks down as seen in the PbO-SiO₂ system. At 66% SiO₂ the Si_{2n}O_{5n}²ⁿ⁻ type ion becomes stable and then Si₂O₇²⁻ ion tends to appear. With further addition of BaO, the absorption band due to the former becomes weaker and that due to the latter becomes stronger. In the CaO-SiO₂ system, the silicate rich in CaO for two liquids range shows the existence of Si₂O₇²⁻ ion as well as vitreous silica as seen in the ZnO-SiO₂ system. Vitreous silica will dissociate into Si_{2n}O_{5n}²ⁿ⁻ type ion between 72~60% SiO₂, and Si₂O₇²⁻ and Si_{2n}O_{5n}²ⁿ⁻ type ion may be stable in the range of 60~50% SiO₂. Below 50% SiO₂ the Si_nO_{3n}²ⁿ⁻ ring type ion may be stable. Addition of Na₂O to SiO₂ will result in a gradual break-down of the three-dimensional network up to 80% SiO₂, and then the three-dimensional complex ion like Si₁₂O₂₇⁶⁻ or Si₁₆O₃₆⁸⁻ may be stable in the range of 80~65% SiO₂, and at the same time, other ion will continue to dissociate into smaller ion group until Si₂O₇²⁻ ion appears at 60% SiO₂. The three-dimensional complex ion like Si₁₂O₂₇⁶⁻ or Si₁₆O₃₆⁸⁻ starts to change into smaller ion at about 60% SiO₂.

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