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STRUCTURAL INVESTIGATION OF MOLTEN AND GLASSY SILICATES BY MEANS OF INFRARED EMISSION SPECTROMETRY

K. Kusabiraki and Y. Shiraishi

Research Institute of Mineral Dressing and Metallurgy, Tohoku University, Sendai 980, Japan

Abstract. In order to clarify the validity of the dummy role of glassy state instead of molten state, the direct method for observing the molecular vibration in molten state has been developed by means of infrared emission spectrometry. The essential feature of this method consists of a combination of the two emission spectra which are obtained from thin and thick layers of the sample on a metal substratum. Transmission spectrum can be obtained from these emission spectra by virtue of the simple relation reported previously.

The infrared emission spectra of molten alkaline silicates were measured in a range of wave number from 25 000 to 400 000 m$^{-1}$ and the transmission spectra obtained in molten state were compared with that of glassy state. The obtained results are summarized as follows:

1. The cooling rate from molten to glassy state in the range of $10^{-2}$ to $10^4$ K/s has little influence on the vibrational spectra of the glassy state thus obtained.

2. Although the general pattern of infrared spectra of molten silicates is quite similar to that of glassy state, it is observed that the vibrational frequencies of molten silicates shift toward the lower frequencies and the band shapes are broader than those of glassy state.

3. From the facts that the temperature dependence of these frequency shifts is linear during the transition from molten to glassy state, it may be concluded that the fundamental structure of silicate anion does not differ seriously in both states.

*Present address : Department of Metallurgical Engineering, Toyama University, Takaoka 933, Japan
1. Introduction.

The direct observation of molten state is very important to clarify the similarity of the structure between molten and glassy state. Though there are some studies reported on the structure of molten silicates by means of X-ray diffraction [1,2,3], Raman scattering [4], and infrared reflection spectrometry [5,6], it is still necessary for better understanding of molten state to accumulate more information by other kinds of direct observations. Thus, the direct method for observation of molecular vibration in molten state has been developed by means of infrared emission spectrometry.

The essential feature of this method consists of a combination of the two emission spectra which are obtained from thin and thick layers of a sample on a metal substratum. Transmission spectrum can be derived readily from the combination of these emission spectra by virtue of a simple relation derived in previous paper [7].

By the application of this method to molten alkaline silicates, distinct vibrational spectra could be obtained [8]. On the basis of the experimental results, the general interpretation of the structure of glassy and molten silicates has been discussed.

2. Experimental.

When a flat sample whose thickness is x, is put on a metal substratum having unity reflectivity, the emissivity of the sample, E, is expressed as follow:

\[ E = \frac{(1-R)[1-\exp(-2\alpha x)]}{1-R \cdot \exp(-2\alpha x)} \]  

where, R and \( \alpha \) are reflectivity and absorption coefficient of the sample, respectively. Let \( E_\infty \) denote the emissivity of the sample having the enough thickness which can be neglected the effect of the transmission of the sample, this \( E_\infty \) reduces to \( (1-R) \) from equation (1). Thus, the transmissivity, T \( (= \exp(-\alpha x)) \), is expressed by the equation (2).

\[ T = \left[ \frac{(E_\infty - E)}{(E_\infty - E + E_\infty \cdot E)} \right]^{1/2} \]  

A experimental apparatus consists of three parts, (i) the furnace in which the sample and the reference black body are heated, (ii) a pair of mirror systems, arranged in symmetric manner, which led the light emitted from both sample and reference black body into a spectrometer, and (iii) a double beam infrared spectrometer, Hitachi IR Spectrometer type 295 (25 000 - 400 000 m\(^{-1}\)). The substratum is made of pt plate, and the reference black body is concave shaped silicon carbide.

The absorption coefficient is quite large in the case of silicate sample, so that the sample with very thin layer, about 1 \( \mu \)m, is required to get a good result. Since the preparation of such a thin sample is very difficult by usual melting method, we took two steps to make the thin layer of the sample. At first, we get a glassy thin film by blowing of the sample melt. Next, we adhere the glassy film onto a hot pt substratum, and then, heat it to melt. By this technique, we can obtain a suitable sample for the infrared spectrum measurement in the acid region of the silicate system, but, in the basic region, can not do it because of low viscosity and the crystallizing tendency of the silicate. Therefore, the measurement has been carried out within the composition range from 20 to 50 mol\% metal oxide for Li-, Na-, and K-silicates.

Fig.1 Infrared emission spectra (A) and transmission spectrum (B) of molten \( \text{Na}_2\text{O}:0.2\text{SiO}_2 \) at 1203 K (solid curves). \( T_g \) is the transmission spectrum of glassy state at room temperature.
3. Results and Discussion.

As an example of the experimental results, the infrared emission and transmission spectra of sodium pyrosilicate in molten and glassy states are shown in Fig. 1. Comparing with the spectra in molten and glassy states, we can easily find that the transmission spectra in both states resemble each other in every absorption bands, but, absorption bands in molten state shift toward lower frequency than that in the glassy state. These results are consistent with that obtained by means of infrared reflection spectrometry by Sweet et al. [5] and by authors [6].

In general, a precise calculation of extinction coefficient from the reflectivity by means of the Kramers-Kronig relation is difficult, because the effect of truncation of the unobservable frequency range is unavoidable. On the other hand, the simple equation (2) has no chance to bring the computation error into the final result [6]. Thus, we may regard the results in Fig. 1 are more reliable than that by reflection spectrometry.

To make more clear the distinction of silicate structure between molten and glassy states, the possibility, whether the structure of glass depend on the quenching speed or not, was tested. Some glass samples prepared in various cooling rates \((10^{-2} - 10^{4} \text{ K/s})\) were measured by KBr tablet method. Obtained results are shown in Fig. 2. In Fig. 2, any meaningful difference between these cooling rates can not be noticed.

Furthermore, detailed experiments on the band shift have been carried out. An example of the spectral observation from molten to glassy state during a continuous descending temperature is shown in Fig. 3. As shown in Fig. 3, we can not observe abrupt change in course of the descending temperature. Thus, we can conclude that...
the structure of silicate anions in glassy state is essentially the same as that of
the melt, in another word, no change occurs seriously on silicate anion species
during the glass transition.

The fact that each absorption band in molten silicate shifts its position to the
lower wave number than that in glassy state, suggests the increasing change in the
bond length between Si and O atoms and/or the decreasing change in the force
constant between them. However, as indicated in Fig.4, which is plotted from availa-
ble X-ray diffraction data \([1,2]\), average interatomic distance between Si and O does
not change in glassy and molten states. So that, the main reason for the band shift
have to be attributed to the decrease of force constant, though this deduction is not
easily understandable. The essential difference between molten and glassy structure
of silicate is in the structural fluctuation. This is evident from both Fig.1 and
fig.4; the broadening of absorption band shown in Fig.1 and the increase of the mean
square root displacement in Fig.4. In this sense, we can state that glass is frozen
liquid.

4. Conclusion.

The infrared emission spectra of molten alkaline silicates were measured and
transmission spectra obtained in molten state were compared with that of glassy
state. The obtained results are summarized as follows:

(1) The cooling rate from molten to glassy state in the range of \(10^{-2}\) to \(10^{0}\) K/s
has little influence on the vibrational spectra of the glassy state thus obtained.

(2) Although the general pattern of infrared spectra of molten silicates is
quite similar to that of glassy state, it is observed that the vibrational frequen-
cies of molten silicates shift toward the lower frequencies and the band shapes are
broader than those of glassy state.

(3) From the facts that the temperature dependence of these frequency shifts is
linear during the transition from molten to glassy state, it may be concluded that
the fundamental structure of silicate anion does not differ seriously in both states.

Reference.

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