

HIGH TEMPERATURE RAMAN SPECTROSCOPIC STUDY OF THE MICRO-STRUCTURE OF SODIUM DISILICATE CRYSTAL, GLASS AND ITS MELT

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Abstract: The micro-structure of $\text{Na}_2\text{Si}_2\text{O}_5$ from room temperature up to 1773 K are studied by high temperature Raman spectroscopy. Temperature-dependent Raman spectra can clearly indicate phase transition. Deconvolutions of complex Raman spectra of crystal and amorphous states (glass and melt) are described. Relative densities of various kinds of SiO_4 tetrahedrons (each Si binding to different number of bridging oxygen) can be qualitatively and quantitatively resolved and varies obviously with temperature. It manifests that high temperature Raman spectroscopy provides a useful tool for the micro-structure research under high temperature and helps to explain properties of silicate glasses and melts.

1 Introduction

Sodium disilicate is main component of various mines, glasses and molten slags. Due to the close relationship between the micro bonding structure^[1,2] and its macro physical and chemical properties, the study of its micro structure under ambient and high temperature has importance. W. Smith^[3] has studied the structure and dynamics of sodium disilicate glass by using molecular dynamic (MD) simulation. For a long time, experimental structure information under high temperature is barely obtained due to insufficient experimental technique under high temperature. Many research works are limited and quenched samples and glasses are usually used instead of melt. M. Handke^[4] pointed out that the structure of non-crystalline samples varies according to their cooling history. In fact, it shows that amorphous materials can never be introduced to completely explain the structure of melt, as was agreed by other researchers^[5].

Raman spectroscopy has been known as an important experimental method of structure studying of materials, and finds its application on silicates^[6]. By analyzing Raman spectra, information about structure order, phase transition and other thermo-dynamic properties can be inferred. Since there is intense optical background of black body radiation, special experimental techniques are necessarily required to acquire the signal among the dense background. Shanghai Enhanced Laboratory of Ferrometallurgy (SELF)^[7] has constructed a macro-Raman setup which uses pulsed Copper Vapor Laser (CVL) as the laser source, time resolved detection system and high temperature resistance furnace based on JY U1000 monochromator. Raman spectra of materials up to 2023K can be attained.

2 Instrumentation

Crystal and glass of $\text{Na}_2\text{Si}_2\text{O}_5$ were prepared from high purity SiO_2 and Na_2CO_3 in analyst grade. The samples compositions were all made by weighing the dried components before fusion. The components were mixed in a mortar and fused in a platinum crucible at 1473 K for 2 hours which was sufficient to obtain a clear and homogeneous melt. $\text{Na}_2\text{Si}_2\text{O}_5$ glass was obtained by quenching the melt in air while the crystal obtained from controlled and slow cooling. Measurements of glass were performed at room temperature while crystal were at various temperature up to 1773 K. Temperature precision was within ± 3 K at all temperatures. Excitation with 510.5 nm radiation from (CVL) was employed. The scattered light was analysed with a JY U1000 double monochromator and detected with a

photomultiplier and photon counting system triggered by a time resolved adjusting system. Raman spectra were stored and subsequently fitted to Gaussian lines shape to define the positions and area of the peaks. The resolution was kept below 3 cm^{-1} at room temperature and below 10 cm^{-1} at high temperature.

3 Results and Discussions

3.1 Comparison of crystal and glass at room temperature

For silicates, Raman bands during $800\sim 1200\text{ cm}^{-1}$ are most important and can be assigned to the symmetric Si-O stretching vibrations of SiO_4 groups with 4, 3, 2, 1 and 0 bridging oxygens (Q^4 , Q^3 , Q^2 , Q^1 , Q^0 species, near 1180 , 1080 , 1000 , 920 , 850 cm^{-1}), respectively. Raman spectra of crystal and glass of sodium disilicate are shown in Fig.1(a) and (b). In Fig.1(a), the strong peak at 1072 cm^{-1} shows that the crystal mainly consists of sheets of Q^3 specie. Two weak peaks at 1021 and 961 cm^{-1} also can be assigned to small amount of Q^2 , Q^1 species which probably are attributed to the edges of the sheets of Q^3 specie. During this wavenumber region, glass of sodium disilicate, as seen in Fig.1(b), has very wide bands due to the well-known disorder of glass. The most intense Q^3 bands of glass shifts to higher frequency due to the inner extra stress which is attributed to the quenching process from the melt. Deconvolution of the high frequency bands can also show three species Q^3 , Q^2 and Q^1 existed in the glass. But the relative abundance of Q^2 and Q^1 are more large than that in crystal. This can be explained by more edges and defects of Q^3 sheets in smaller sizes.

Medium frequency range bands $400\sim 800\text{ cm}^{-1}$ are assigned to bending vibrations of Si-O-Si. Large FWHH (Full Width at Half Height) of glass bands illustrate a distribution of bond lengths and angles. Glass shows a wavenumber shift from crystal, 517 cm^{-1} to 571 cm^{-1} also due to the inner extra stress in glass. Weak peak at 763 cm^{-1} of crystal and weak band at 772 cm^{-1} of glass are caused by bending vibrations of Q^1 and Q^2 species. There is a completely different in low frequency range ($<400\text{ cm}^{-1}$). Peaks 384 cm^{-1} and 337 cm^{-1} of crystal can be attributed to the vibrations of Na-O and 149 cm^{-1} , 223 cm^{-1} and 270 cm^{-1} are caused by structure order in large distance scale which disappear in glass.

3.2 Temperature dependence from crystal to melt

Sodium disilicate crystal is selected to be heated in steps (more than half an hour pause at each step) and is measured in high temperatures from $298\sim 1773\text{ K}$. As seen in Fig.2 (spectrum of 500 K is not shown), all the bands are getting broaden and some weak peaks which are well resolved in room temperature, especially the low frequency bands, become faint and disappear with the increasing temperature. One can distinguish the spectrum of 1143 K from other spectra, since its characteristic of $500\sim 600\text{ cm}^{-1}$ region, which is overlapped by spectra of two phases, just records and illustrates the phase transition process from solid state to liquid melt.

By assuming that there are several species in the high wavenumber vibrational region, curves fittings are introduced to resolve the measured spectra. Fig.3 shows a typical deconvolution of the spectrum of the melt at 1473 K with Q^3 , Q^2 and Q^1 species. At different temperatures the trends of the frequencies of bands are shown in Fig.4. Either in the crystals or in the melts, there are slight redshift for the frequencies of three species except during T_g ($\sim 1000\text{ K}$) to T_m ($\sim 1140\text{ K}$) temperature region, drastic frequency changes of 961 cm^{-1} band and abnormal enhancement of frequency of 1072 cm^{-1} band can be clearly found. Those characteristics are the evidences of phase transition of $\text{Na}_2\text{Si}_2\text{O}_5$ from solid to liquid state. But the frequency deviation of each specie can also be considered much less than to be thought as

other specie.

The actual relative abundance of individual structural units in crystal, glass and melt as a function of temperature can be obtained from the Raman spectra. But the calibration of the deconvoluted and integrated Raman intensities of appropriate bands is needed, and the sensitivity factors which is mainly resulted from scattering cross section for different Q^n specie are defined in elsewhere^[8]. It is convenient to assume S_Q^2 as 1, accordingly S_Q^3 and S_Q^1 have been measured and calculated as 0.352 and 1.81. A method of inner standard was used to figure out the relative factors by comparing Raman spectra of a series of mixtures which consist of some simple binary sodium and calcium silicates and inner standard $NaNO_2$. That is, Q^2 specie with S_Q^2 as 1 is more sensitive than Q^3 specie ($S_Q^3 = 0.352$), but less sensitive than Q^1 specie ($S_Q^1 = 1.81$) in intensity or area of Raman bands provided the same mole fraction of each specie may be considered. It's noted that the data 0.352 for S_Q^3 is approximately the same as $\theta_{Q^2}/\theta_{Q^3} = 1/2.92 = 0.342$, which is independently summarized by Mysen^[9] by considering the combined ^{29}Si NMR and Raman data. And the data deviation may be caused by different optical and detection systems.

As also mentioned by Mysen^[10], two assumptions should be considered previously when applying these sensitivity factors to crystals, glasses and melts. One is that the sensitivity factors are insensitive to the different metal cation, the other is that the sensitivity factors are insensitive to the temperature at which the Raman spectra were obtained. It is found that even though in principle it would be expected that the type of metal cation should affect the Raman intensities, a comparison of calibrations derived from the spectra of glasses in the systems Na_2O-SiO_2 and K_2O-SiO_2 revealed no differences within the errors.

At temperatures less than 1673 K, there are just four Q^n species ($n=1, 2, 3$ and 4) existed in the crystals and melts of $Na_2Si_2O_5$, with the above reasonable assumptions, then,

$$X_Q^n = A_Q^n / S_Q^n \quad (n = 1, 2 \text{ and } 3) \quad (1)$$

Where X_Q^n , A_Q^n and S_Q^n is the mole fraction, Raman band area and sensitivity factor of Q^n specie, respectively. Because Q^4 specie is more less sensitive than Q^3 specie, its Raman band has not appeared under these temperatures from the deconvoluted spectra even though there is small amount of Q^4 specie. By considering simple mass and non-bridging oxygen ($NBO/Si = 1$) balance, the following equation can be obtained.

$$X_Q^4 = X_Q^2 + 2X_Q^1 \quad (2)$$

X_Q^1 , X_Q^2 , X_Q^3 and X_Q^4 are then normalized to denote the mole fractions with the overall SiO_2 as unit. While at temperatures of 1673 K and 1773 K, Raman band of Q^0 specie appears. So there are all the five species existed in the melts. S_Q^0 is estimated as 2.85 by the extrapolation from S_Q^1 , S_Q^2 and S_Q^3 series, as is also reasonable in some other investigations. Then, accordingly,

$$X_Q^4 = X_Q^2 + 2X_Q^1 + 3X_Q^0 \quad (3)$$

Fig.5 shows that the normalized distribution of X_Q^n with the increasing temperature. One can find that below the melting point of $Na_2Si_2O_5$, Q^3 specie has a large amount of above 90% mole fraction while the sum of other species less than 10%. But it is obvious to note that the amount of Q^4 specie is larger than that of Q^1 and Q^2 species. After temperature of T_g (~1000 K), a small decrease of Q^3 specie while all the other species showing a little bit increase can be found. A drastic changes happened during the melting process with Q^3 specie sudden decreasing from about 90% to 75~80% while Q^4 specie uprising from about 6% to

13~15%. Then, after the crystal was melt, all the Q^n species appeared to remain relative stable until at temperature of about 1573 K. Above this temperature, Q^4 , Q^2 and Q^0 species showed a linear increasement while Q^3 and Q^1 species appearing a linear decrease. At the highest temperature that we obtained, the mole fractions are about 22.3%, 63.5%, 8.0%, 4.1% and 2.0% for Q^4 , Q^3 , Q^2 , Q^1 and Q^0 species, respectively.

It indicates that there are several equilibriums existed in solid and liquid states of $Na_2Si_2O_5$. The following equation demonstrate the reactions between Q^n species. And with

$$2Q^n = Q^{n+1} + Q^{n-1} \quad (n = 1, 2, 3) \quad (4)$$

the temperature increasing, decompositions are the main trend due to endothermic reactions, that is, there are more Q^n species in higher temperature. The high wavenumber of Raman spectrum of $Na_2Si_2O_5$ glass is also deconvoluted and assigned to different Q^n species. There are about 11.4%, 80.0%, 5.9%, and 2.7% mole fractions for Q^4 , Q^3 , Q^2 and Q^1 species in the glass, respectively. The Q^n distribution in glass is approximately the same as that of just around melting point, 1143 K, but other two structural characteristics should be noted that they are greatly different in frequencies and FWHH of the individual deconvoluted Raman band. The glass bands show a 10 to 40 cm^{-1} shift to higher frequencies, which is due to decreased bond lengths due to the thermal contracting of the medium. And the melt bands are broader than in the glass. This wider distribution of the modes in the melt bands shows that the disorder of the melt is greater than that of the glass.

4 Conclusions

Differences in structure between $Na_2Si_2O_5$ crystals, glass and its melts are obvious. Crystal experienced a small change in Q^n distribution from above T_g and greatly rearranged them at T_m . Melt sustained a relative stable Q^n distribution from above T_m to about 1573 K. It is clear that melt still underwent to rearrange its structure units at higher temperature, and more Q^n species would be yielded with the increasing temperature. Although Q^n distribution of the glass is similar to that of melt of around T_m , it should be noted that the melt structure shows a greater disorder than that of the glass when might extrapolate the knowledge of silicate glasses to silicate melts.

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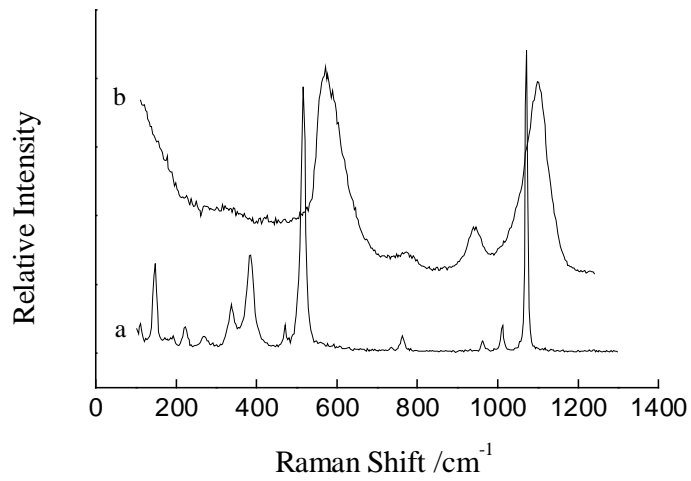


Fig.1 Raman spectra of Na₂Si₂O₅ crystal (a) and glass (b) at room temperature

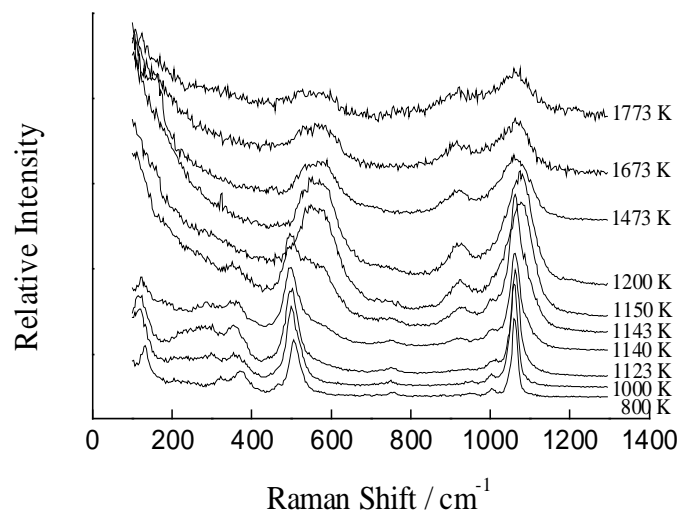


Fig.2 High temperature Raman spectra of Na₂Si₂O₅ crystals and its melts

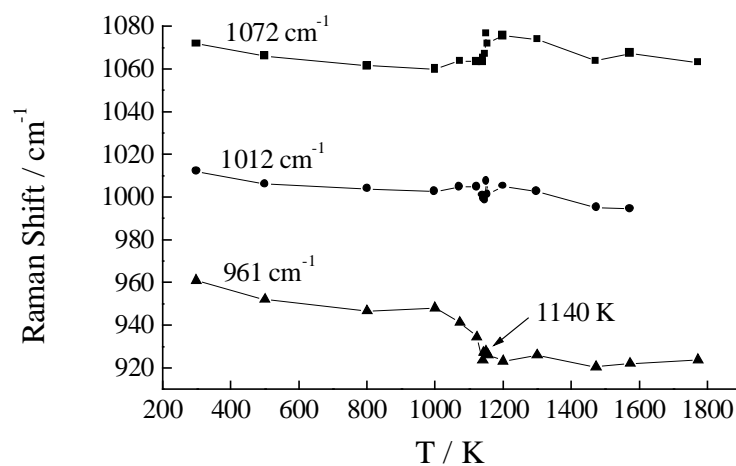


Fig.3 Temperature dependence of stretch vibrational frequencies

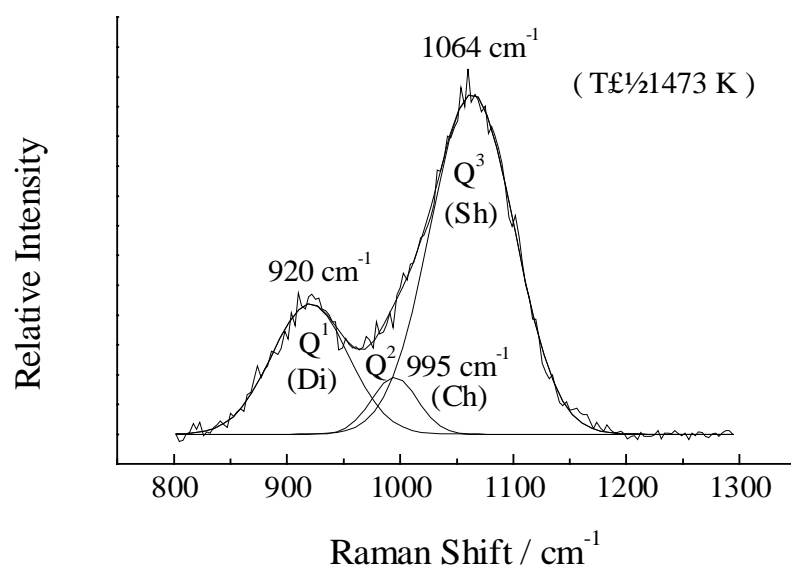


Fig.4 Gaussian deconvolution of stretch vibrational band

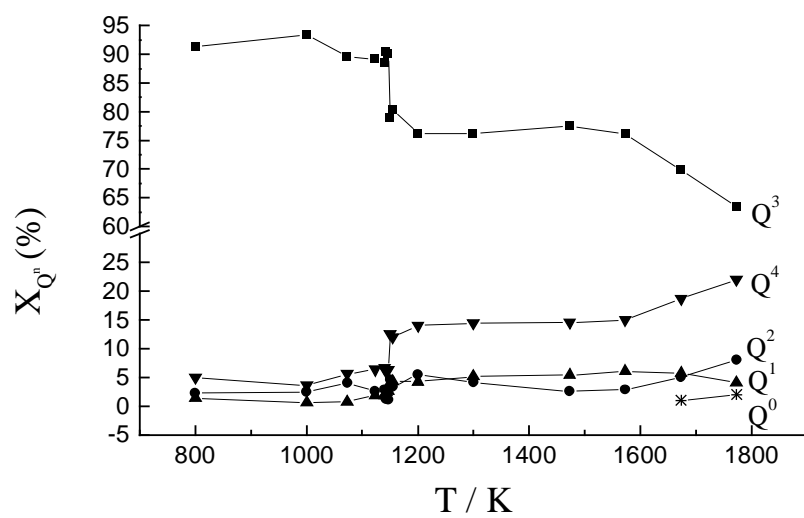


Fig.5 Temperature dependence of normalized Qⁿ abundance