Isomorphic representations of hyperfine structure of binary silicates by interior stress, vibrational wavenumber and spacial fractional dimension

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Abstract. Stress index of tetrahedron (SIT) was defined to describe the topological connectivities among various silicon-oxygen tetrahedra (SiOT) in anionic clusters of binary silicate crystals, glasses and melts. It was found that the value of SIT was well correlated with the wavenumber of Raman active symmetric stretching vibration of non-bridging oxygen of SiOT. And also the spatial fractional dimension of hyperfine structure was introduced while comparative analysis being made with the value of SIT. It can be concluded that the concepts of SIT, vibrational wavenumber and spatial fractional dimension were inherently and holographically correlated and exhibit isomorphic representations of complex structure of binary silicates. Experimental Raman spectra of binary silicates with different alkali cation were investigated. It was demonstrated that alkali cation has little effect on the vibrational wavenumber of symmetric stretching of non-bridging oxygen (NBO) of SiOT, but remarkably affects its Raman active optical cross section, as was consensus resulted from *ab initio* calculation. It also can be concluded that the spatial fractional dimension of binary silicate is predominantly determined by the hyperfine structure of the anionic clusters and little affected by alkali cation, although the species of anionic clusters and their distributions were originally assigned by the content of alkali oxides.

1. Introduction
The crystals, glasses and melts of silicates have been extensively applied in many fields and their micro-structure study has gained much attention [1-4]. In recent years, lots of theoretical calculations and experimental methods have been used in the studying of the structure of silicates. They are classical molecular mechanics force field (MMFF) [5], quantum chemistry (QC) [6], molecular dynamics (MD) [7], Monte Carlo (MC) [8], X-ray diffraction [9], nuclear magnetic resonance (NMR) [10], extended X-ray absorption near edge structure (XANES) [11], infrared (IR) and Raman spectroscopy [12, 13].

Raman spectroscopy was widely recognized as one of the key method to study the micro structure of materials. And high temperature Raman spectroscopy (HTRS) [13] technology is drawing more attentions for being an effective tool to study the structure of melt under high temperature. Raman
spectroscopic study of silicates could contribute to the knowledge of structure in various states and the thermodynamic properties of silicates [14, 15].

Previous studies suggested that the vibrational wavenumber of non-bridging oxygen (NBO) symmetric stretching in silicate Raman spectra is approximately monotonically related to the primary structures of $Q_i$ species, which is accepted by most researchers. Sharma et al. [16], Iguchi et al. [17] and Akaogi et al. [2] demonstrated that the Raman-active peaks around 1100, 1000, 900 and 850 cm$^{-1}$ correspond to the NBO symmetric stretching vibration of the silicon-oxygen tetrahedron (SiOT) with 3, 2, 1 and 0 bridging oxygens, or $Q_3$, $Q_2$, $Q_1$ and $Q_0$ species, respectively. So far this idea of qualitative identification is still the common consensus in Raman spectral studies of the microstructure of silicates. However, careful observations [18-22] showed that this vibrational wavenumber is also related to the different structural phases and can be modified substantially by various ring constructions. This inclines to view that Raman-active modes of NBO symmetric stretching in the high-wavenumber range comprise the information on both the types of SiOTs and their connectivity and configurations. However, until now the delicate and widely-accepted correlation with microstructure was still unclear.

2. Experimental
A newly constructed ultra high temperature Raman spectrometer [23] by using pulsed laser based on JY LabRAM HR and enhanced by Intensified Charge Coupled Device (ICCD) detector was used to record in-situ Raman spectra of various inorganic materials and their melts under ultra high temperature.

Crystal samples of binary silicates were prepared from reagent grade SiO$_2$ and M$_2$CO$_3$ (M=Li, Na, K, Rb and Cs). The sample compositions were obtained by weighing the dried components before fusion. The components were mixed in a mortar and fused in a Pt-10%Rh alloy crucible at 1473-1873 K for 2 h which was sufficient to obtain a transparent, colourless and a visibly homogeneous liquid. Crystal samples were obtained by adequate cooling methods according to the phase diagram of binary silicate while the melt being quenched in air to obtain corresponding glass samples. Raman measurements were performed at room temperature and various high temperatures. The resolution of Raman shift was $< 3$ cm$^{-1}$ at room temperature and $< 10$ cm$^{-1}$ at high temperatures.

3. Results and discussion
3.1. Hyperfine notation for SiOT and stress index of a tetrahedron (SIT)
In order to describe the SiOT with its local environment or hyperfine structure information in detail, a new notation [24] was proposed and denoted $Q_{i,j,k,l,m}$, where $i$ is the number of bridging oxygens (BOs) of the central SiOT, concerned the superscripts $j$, $k$, $l$ and $m$ corresponding to $Q_j$, $Q_k$, $Q_l$ and $Q_m$ are the adjacent SiOTs and the subscripts $t$, $q$ and $h$ corresponding to the ring types of trigonal, quadrangle and hexagon in which the SiOT concerned participates and $n_1$, $n_2$ and $n_3$ are the number of respective rings of the polygon. This notation gives more delicate microstructure information around the SiOT concerned prior to only five types of $Q_i$ species. Also, the difference which reflects between different SiOTs might be applied to explain diversity and discrepancies emerging in spectra and macro properties in practice.

The stress index of tetrahedron (SIT) of SiOT was empirically defined as follow [24],

$$ SIT = ^1\chi + \alpha R $$

$$ ^1\chi = \frac{1}{i} \sum_{j=1}^{i} \sqrt{Q_j Q_{i,j}} $$

$$ R = \frac{1}{n_j - 2} $$
where $\chi'$ is the first-order molecular connectivity index [25] (MCI) of SiOT, and $Q_i$ can also be considered as the zero-order MCI, that is, $\chi$. In the case of equivalent connection of SiOTs, the value of $\chi'$ is the same as $Q_i$. While unequivalent connections appear, for example, the value of $\chi'$ is given by the following expression:

$$\chi' = \frac{1}{3}(\sqrt{3 \times 3} + \sqrt{3 \times 4} + \sqrt{3 \times 4}) = 3.309$$

(4)

on the assumption that the $Q_j$ species concerned is connected with one $Q_i$ and two $Q_i$ species. $a$ and $R$ are the proportionality coefficient and the contribution of the ring, respectively. It is reasonable that the stress in a ring is related to the internal angle or number of sides of a regular polygon assuming all side lengths to be the same. Since the sum of the degree of all the internal angles is $(n-2)\pi$, it can be assumed that the stress contribution of a ring is the function of $(n-2)$. $n_j$ is the number of all the $Q_i$ species making up the jth ring in which the SiOT concerned participates, and $m$ is the overall number of participating rings. A single SiOT with more BOs or smaller ring it participates can be estimated to have a larger value of SIT, showing more interior stress induced by its microscopic environment.

3.2. Symmetric stretching vibration of NBO of SiOT

Model clusters used in calculation were chosen based on the consideration of varying $Q_i$ species, different rings of SiOTs construction. QC calculation software of Gaussian98W [26] was used and restricted Hartree-Fock (RHF) calculation method with the basis sets of 6-31G(d) was applied to optimize the structural geometry of sodium modified model clusters. Wavenumbers of Raman-active modes and Raman optical activity (ROA) were calculated under the same method with the same basis set after geometric optimization. The results [24] show the comparison of the calculation result and relevant experimental data. There is a good correlation. This demonstrates that $Q_i$ species are not the exclusive factor to determine the NBO symmetric stretching vibrational wavenumber.

Based on the above considerations, probable delicate types of different SiOTs within clusters in practical binary sodium silicates are shown in Figure 1. Each characteristic SiOT has its own corresponding and specific SIT value and symmetric stretching vibrational wavenumber of NBO. It offers a more informative and delicate description of SiOT arrangements inside the silicates. Curve fitting should be introduced to deconvolute the reduced and heavily overlapped spectra. It should be noticed that the deconvolution method aided by Origin 6.0 software is not be ideal for processing with more spectral peaks, so an individual peak may still comprise of several delicate SiOT species. However, it is interesting to make the comparison of microstructure between the glass and its melt. The vibrational wavenumbers of all the individual deconvoluted peaks of glass are higher (about ~20-40 cm$^{-1}$) than that of the counterpart of its melt due to temperature-induced shift [24]. Also the corresponding full width at half height (FWHH) of the individual peaks and the whole Raman band are smaller than those of the melt because of the larger distribution of interior coordinates of hyperfine

![Figure 1](image-url). Correlation among SITs, wavenumbers of NBO symmetric stretching vibration and probable hyperfine structure types of SiOTs within clusters in practical binary sodium silicates.
structure inside the various clusters of the melt at high temperature. The relative area of the individual peak does not correlate pro rata the density of delicate SiOT species because of different ROA for different hyperfine species.

3.3. Spacial fractional dimension of silicates network
Four types of silicate crystals of $2\text{Na}_2\text{O} \cdot \text{SiO}_2$, $\text{Na}_2\text{O} \cdot \text{SiO}_2$, $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ and pure $\text{SiO}_2$ with characteristic spacial configurations were used to illustrate the correlation between their spacial fractional dimensions and the newly defined SIT. They are corresponding to isolated monomer, infinite chain, sheet and network, respectively. It is well accepted that they should be exactly 0, 1, 2 and 3, respectively, as the value of spacial fractional dimensions.

On the other hand, the value of SIT for these four types of silicates can be calculated according to its structure characteristics. They are 0, 2 and 3.75 with the notation of $Q_0$, $Q_{22}$ and $Q_{333}$ for $2\text{Na}_2\text{O} \cdot \text{SiO}_2$, $\text{Na}_2\text{O} \cdot \text{SiO}_2$ and $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$, respectively. As to pure $\text{SiO}_2$, although there are different isomers, it has little discrepancy for the calculated SIT values for common stable crystals with only four-oxygen-coordinated silicon inside. The SIT value of cristobalite is 5.5 with the notation of $Q_{4444}$ and that of β-quartz is 5.667 (for β-quartz) with the notation of $Q_{4444}$, in which there are four octagons in additional to four hexagons.

Figure 2 demonstrates that a fairly good linear correlation between spacial fractional dimensions of silicates and the SIT values. Their relationship manifests that both concepts of spacial fractional dimension and SIT of silicates, representing macro and micro characteristics, respectively, are inherently and holographically correlated.

3.4. The cation effect on Raman spectra
Although different kind of cation has little effect on the symmetric stretching vibrational wavenumber of NBO of SiOT in the high-wavenumber range, it doubtless influences the prediction of vibrational wavenumbers. The cation effect might be realized by its varying electronegativity and ion radius and will result in an equilibrium microstructure of various anion clusters in melts and glasses.

Figure 3 shows that a typical example of five different binary alkali silicates which have the same mole fraction (0.75) of $\text{SiO}_2$. It can be seen clearly that the Raman intensity or peak area in the high-wavenumber range increases with the increasing radius of the cation. QC ab initio calculation was also made to study the cation effect with those clusters [24] combined with different cations. This enhancement can be explained by less charge transfer along the Si-O$_{ab}$ bond, that is, there is more covalent percentage on the bond. Thus it reveals that Raman scattering cross section increases by the order of Li, Na, K, Rb and Cs both by experimental and calculation results.

4. Conclusions
It can be concluded that the value of SIT was well correlated with the wavenumber of Raman active symmetric stretching vibration of NBO of SiOT. And also the spatial fractional dimension of hyperfine structure was introduced. It can be concluded that the concepts of SIT, symmetric stretching wavenumber of NBO of SiOT and spatial fractional dimension were inherently and holographically correlated and exhibit isomorphic representations of complex structure of binary silicates. Experimental Raman spectra of binary silicates with different alkali cation were investigated. It was demonstrated that alkali cation has little effect on the vibrational wavenumber of symmetric stretching of NBO of SiOT, but remarkably affects its Raman active optical cross section, as was consensus resulted from \textit{ab initio} calculation. It also can be concluded that the spatial fractional dimension of binary silicate is predominantly determined by the hyperfine structure of the anionic clusters and little affected by alkali cation, although the species of anionic clusters and their distributions were originally assigned by the content of alkali oxides.

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