

THE CORRELATION OF RAMAN SPECTRA, VIBRATIONAL DENSITY OF STATES AND COUPLING COEFFICIENTS OF CALCIUM SILICATE MELTS

G. C. Jiang, Y. Q. Wu, J. L. You and H. Chen

Shanghai Enhanced Laboratory of Ferro-Metallurgy, Shanghai University, Shanghai 200072, China; E-Mail: gcjiang@online.sh.cn or wu_yq1222@163.com

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Abstract: The Raman spectra (RSs), vibrational density of states (VDOSs) and corresponding coupling coefficients (CCs) of silicate melts were theoretically calculated from a newly method and compared with each other to explore the properties of vibrational spectra. The sameness of lineshapes of partial CCs gives a strong conclusion that the partial CCs are the intrinsic characteristics of Si-O tetrahedral units and independent of composition.

Recently, the high-temperature Raman spectra (HTRS) technique has been achieved great developments [1]. With the application of this technique, the Raman spectra (RS) of high-temperature melts, e.g. silicate and borate, can be obtained. One of the following steps of this research is to reduce the RS into the corresponding vibrational density of states (VDOS). But, the joint between RS and VDOS is still not clear, especially the spectra of melts. With a newly developed method [2], we can theoretically study the corresponding VDOS, including the partial VDOSs of Si-O tetrahedra denoted with Q_i where i is the number of bridging oxygen and the total.

Summarized with a word, this method is the combination of MD simulation, eigen vibrational analysis and Raman intensity calculation. Firstly, NPT molecular dynamics simulation was performed and the empirical two-body Born-Mayer-Higgins potential was applied. The fictitious temperature was set at 2000K. The simulated structural properties have been compared with experiments and a very good agreement was obtained [3]. After that, 2500 equilibrated configurations were extracted at the rate of one configuration per 120 steps and each of them was decomposed into five defined Si-O tetrahedra, i.e. Q_i . Then, each Q_i was analysed by solving the GF matrix and the relative Raman intensities was also calculated. Finally, the RS was obtained by accumulating all the data of frequencies and corresponding Raman intensities, while for the VDOS, only the frequencies are needed.

Usually the following equation is used to exhibit the relation of VDOS and other kinds of spectra:

$$I(\omega) = C(\omega) \rho(\omega) \quad (1)$$

Where, $I(\omega)$ is the spectral intensity of either IR or RS or INS (inelastic neutron scattering). $C(\omega)$ is the so-called coupling coefficient. It was considered that INS might be used to give directly the measure of VDOS. In fact, this is an approximation due to that the coupling constant of INS is not a constant but a slowly varying function of the frequency. In addition, so far the experiments were merely carried out for some simple compounds as SiO_2 and so on. This situation promotes some researchers to develop the way of calculating VDOS. The computation methods they used and their principle results can be found from the review of Galeener etc. [4] and Zotov etc. [5].

As an application, the VDOSs, RSs and corresponding CCs of CaSiO_3 melt, including the partials and totals, are shown in the Fig. 1. From Fig.1, following conclusions and corresponding interpretations can be achieved by comparing the RS, VDOS, and CC with each other. Generally, the partial and total RSs have two obvious peaks located at medium- and high-frequency regions except Q_0 and Q_4 . The partial RS of Q_0 has no peak in the medium-frequency region because there is no vibrational mode in this region for the partial VDOS. Oppositely, the partial RS of Q_4 has also no peak in the high-frequency region, while its corresponding VDOS and CC reveal the completely different reason from Q_0 that although there are great deal of vibrational modes but their CCs are very small and close to zero. As the short sticks point in Fig. 1, the lineshape of CC shows us that

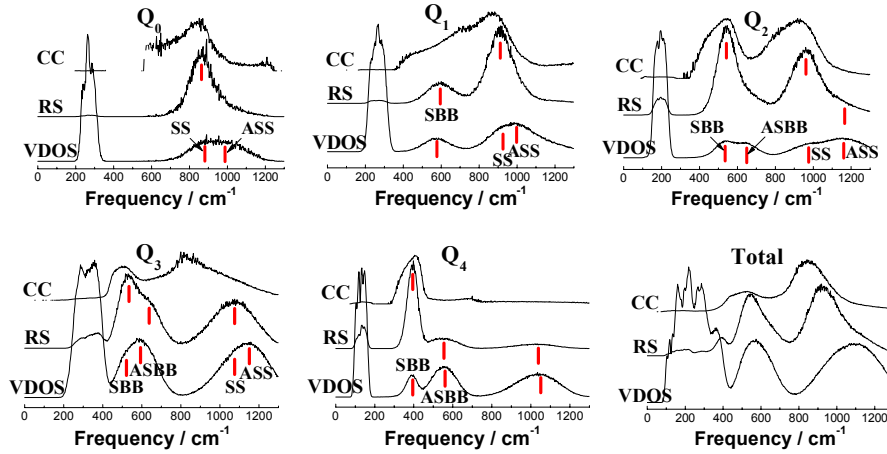


Fig. 1. The calculated partial and total RSs, VDOSs and CCs of CaSiO_3 melt

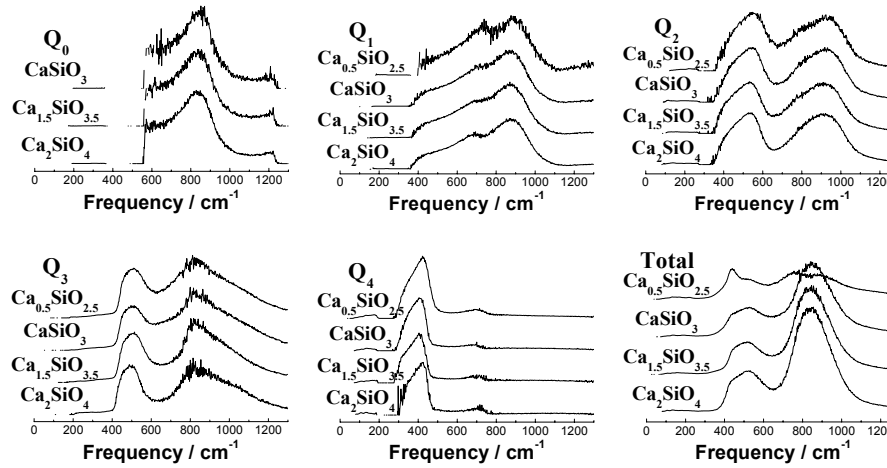


Fig. 2. The partial coupling coefficients of Q_i and total coupling coefficients of the samples

scattering coefficient, sometimes called Raman scattering factor, can also be achieved from this method. Table 1 lists two calculated and experimental ratios of S_3/S_2 and S_2/S_1 and the good agreement can be achieved. It must be noted that the value of Mysen and Frantz [7] is achieved by referencing the NMR data of Stebbins [8] and You et al. [6] used the inner reference of NaNO_2 powder.

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the Raman intensity of asymmetric vibrational mode (ASS or ASBB) should be much weaker than that of symmetric mode (SS or SBB).

Certainly, the RS coupling coefficient $C(\omega)$ mentioned in Eqn. (1) meaning the Raman intensity averaged for all the modes at the frequency may be easily gained if the co-related VDOS and Raman spectra have been calculated. The obtained RS coupling coefficients are shown in Fig. 2. One can also find from Fig. 2 that the $C(\omega)$ s of various samples are different but the partial $C(\omega)$ of Q_i has no change in different samples. This is because the mole fractions of every kinds of tetrahedral in various samples are different.

As an integral of $C(\omega)$, the Raman

TABLE 1. The comparison of the calculated S_3/S_2 and S_1/S_2 With the experimental results

	S_3/S_2	S_1/S_2
Calculated	0.37	0.21
Experimental of You [6]	0.35	0.18
Experimental of Mysen [7]	0.34	-