

STRUCTURE STUDIES OF SILICATE GLASSES BY RAMAN SPECTROSCOPY

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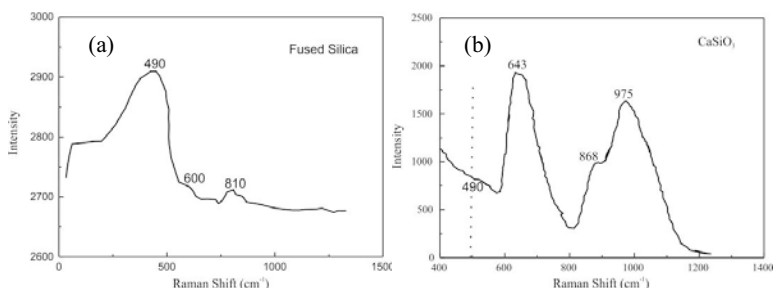
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Abstract

Silicate slags are widely used in many pyrometallurgical processes. The physiochemical properties of the slags, particularly viscosity, are closely related to their internal structures at operating conditions. To fundamentally investigate the correlation between slag structures and viscosities, the glassy samples in SiO₂-CaO, SiO₂-CaO-MgO and SiO₂-CaO-Al₂O₃ systems were prepared by directly quenching to water. The quenched slags that maintain structures at high temperature were analyzed quantitatively by Raman spectrometer. The appropriate conditions of Raman spectroscopy measurements have been evaluated to obtain a better spectra for quantitative analysis. The proportions of four types of Si with different coordination can be clearly revealed from the analyses of the Raman peaks. The viscosities of the slags are correlated with the changes of the characteristic peak positions and areas.

Introduction

Extensive studies on the structures of the SiO₂-CaO based melts have been performed using Raman spectroscopy. The intensity and shift of Raman bands with the silicate structural units were linked in the present study. The complex silicate melts are composed of different Si units, which can be clearly revealed from the analysis of the Raman bands [1]. From the Raman spectrum of pure silica (Figure 1a) [2], the bands at around 490 cm⁻¹, 600 cm⁻¹ and 800 cm⁻¹ are assigned to the vibrations of 4-fold, 3-fold ring and defected silicate structure respectively [3]. In the Raman spectrum of CaSiO₃ glass in Figure 1b [4], the diminished band at 490 cm⁻¹ and enlarged band at 643 cm⁻¹ indicate the degradation of 4 folded ring to 3 folded ring silicate structure. From the Raman spectra of Ca₂SiO₄ (Figure 1c) and Ca₃SiO₅ (Figure 1d), the dominant bands at 910 cm⁻¹ and 850 cm⁻¹ are defected silicate unit and the bands located 490 cm⁻¹ and 600 cm⁻¹ shrink and disappear.



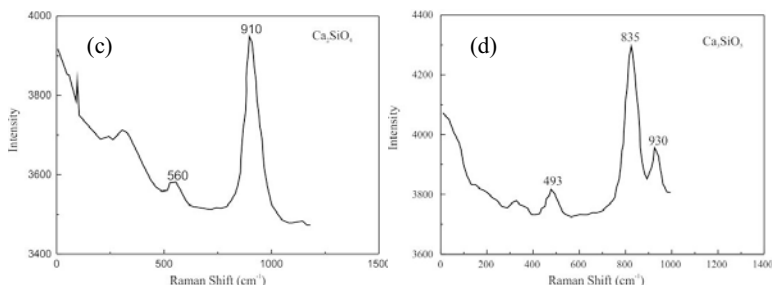


Figure 1. Raman spectrum of (a) fused pure silica [2], (b) CaSiO_3 [4], (c) Ca_2SiO_4 [5] and (d) Ca_3SiO_5 [6]

In present study, the quenched slag samples were analyzed by Raman spectrometer to investigate the degree of polymerization (DP) of SiO_2 -CaO based systems with additions of MgO or Al_2O_3 .

Methodology

The quenched slag samples were prepared for the SiO_2 -CaO, SiO_2 -CaO-MgO and SiO_2 -CaO- Al_2O_3 systems. Approximately 0.25g mixture was prepared by mixing the required chemicals with grinding. The details of equilibration experiments were described in the previous publication [7]. In brief, the sample in graphite crucible was equilibrated in Ar for 2 hours. After equilibration, the sample was instantly quenched into water to maintain its microstructure at high temperature. Raman spectroscopy and electron probe X-ray microanalysis (EPMA) were conducted for each sample and the results of EPMA are shown in Table I.

Table I: Experimental conditions and EPMA results

Chemical Systems	Temperature ($^{\circ}\text{C}$)	EPMA Results (mol%)			
		SiO_2	CaO	Additive	CaO/ SiO_2
SiO_2 -CaO	1500	66.3	39.7	0	0.6
	1500	58.7	41.3	0	0.7
	1553	52.5	47.5	0	0.9
	1466	47.8	52.2	0	1.1
SiO_2 -CaO-MgO	1500	47.3	47.7	4.6 (MgO)	1.0
	1500	44.9	46.1	9 (MgO)	1.0
	1500	43	42.7	14.3 (MgO)	1.0
	1500	39.6	40.6	19.8 (MgO)	1.0
SiO_2 -CaO- Al_2O_3	1500	47.5	47.4	5.1 (Al_2O_3)	1.0
	1500	45	45.4	9.6 (Al_2O_3)	1.0
	1500	42.4	42.6	15 (Al_2O_3)	1.0

The quenched samples were mounted in epoxy resin and polished for Raman spectroscopy measurements (Ranishaw, Wotton-under-Edge, UK). The Raman spectra were recorded at room temperature in the frequency range of 100 - 1500 cm^{-1} using argon ion laser (514 nm).

With the studies of SiO₂-CaO glasses and silicate polymer theory, the major bands were assigned to different structural units, as shown in Table II [3]. The details of peak deconvultion were described in the literature [8] and utilized in the present study.

Table II. The descriptions of Raman bands (NBO/T=Non-bridging oxygen/total silicate)

Peak	Raman Shift (cm ⁻¹)	NBO/T	Polymer Theory
D1	480-500	NA	4-fold ring
D2	590-610	NA	3-fold ring
Q1	850-880	NBO/T=4	SiO ₄ with zero bridging oxygen
Q2	900-930	NBO/T=3	Si ₂ O ₇ with one bridging oxygen
Q3	950-980	NBO/T=2	Si ₂ O ₆ with 2 bridging oxygen
Q4	1040-1060	NBO/T=1	Si ₂ O ₅ with one bridging oxygen

Results and Discussions

Raman Spectrum Analyses

The addition of CaO into silica dramatically influences the structure of silicate melt. Figure 2 shows the Raman spectra for the SiO₂-CaO system with CaO/SiO₂ ranging from 0.6 to 1.1. As shown in Figure 2a, for each spectrum there are two major bands located in 580-680 cm⁻¹ and 800-1200 cm⁻¹ regions. The D1 band is not found in SiO₂-CaO, SiO₂-CaO-MgO and SiO₂-CaO-Al₂O₃ systems. The two bands were further deconvulted into 2 and 4 peaks respectively as shown in Figure 2. The D3 peak was reported from non-linear least squares minimization method [8], which may be defined as a kind of lower order silicate ring structural unit. The locations and area occupancies were summarized in Table III.

Table III. Peak shift and relative area fraction of each peak in SiO₂-CaO Raman spectrum

CaO/SiO ₂	D2	D3	Q1	Q2	Q3	Q4
	Peak Shift					
0.6	589.8	633.8	866.6	910.5	959.7	1061.6
0.9	624.3	667.0	864.7	913.2	963.1	1027.4
1.1	642.0	682.0	848.5	898.3	962.2	999.5
	Peak Area					
0.5	0.090	0.174	0.014	0.027	0.240	0.454
0.9	0.068	0.169	0.132	0.061	0.221	0.320
1.1	0.066	0.144	0.143	0.204	0.181	0.261

When the ratio of CaO/SiO₂ is increased from 0.6 to 1.1, the peaks D2 and D3 report 589.8 - 642 and 633.8 - 682 cm⁻¹ shifting respectively, which may be caused by the decrease of Si-O-Si bond angles [3].

It is assumed that the area of each peak is proportional to the concentration of structural unit. The area of each peak is plotted against CaO/SiO₂ ratio as shown in Figure 3. It is noticeable that Q4 are most abundant unit at CaO/SiO₂ ratio of 0.5. The area fractions of the D2, D3, Q3 and Q4 peaks continuously decrease, and the fractions of Q2 and Q1 increase with increasing CaO/SiO₂

ratio. This tendency qualitatively indicates that the silicate networks are depolymerized with addition of CaO.

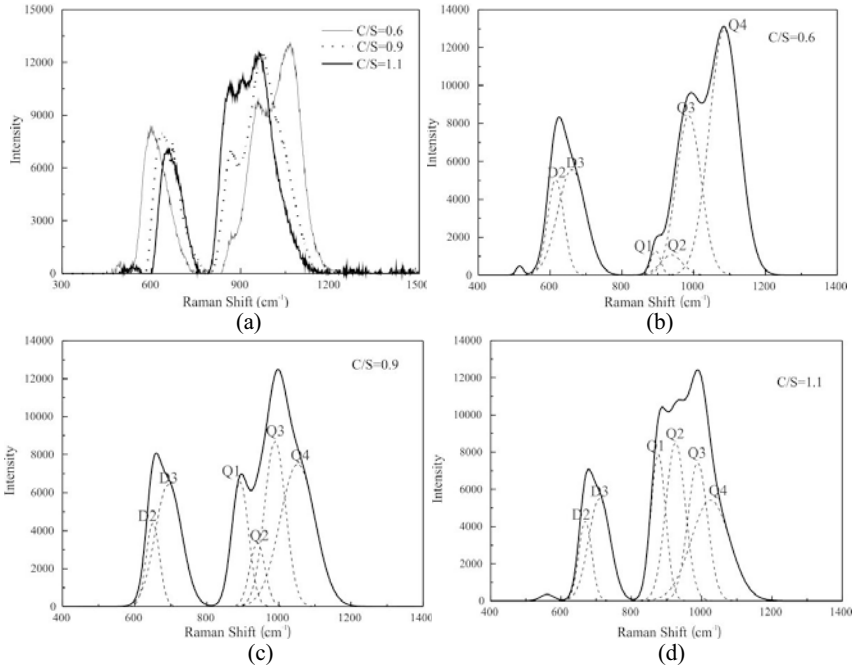


Figure 2. Raman spectra of SiO₂-CaO system at different CaO/SiO₂ molar ratios, (a) All (b) C/S=0.6, (c) C/S=0.9 and (d) C/S=1.1

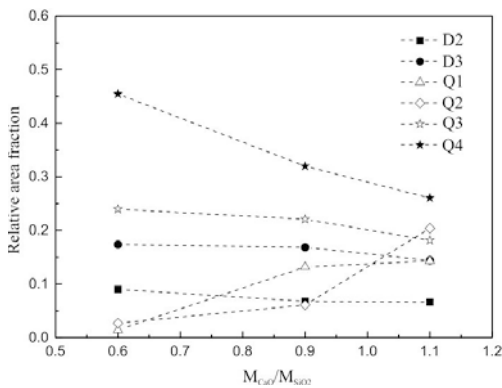


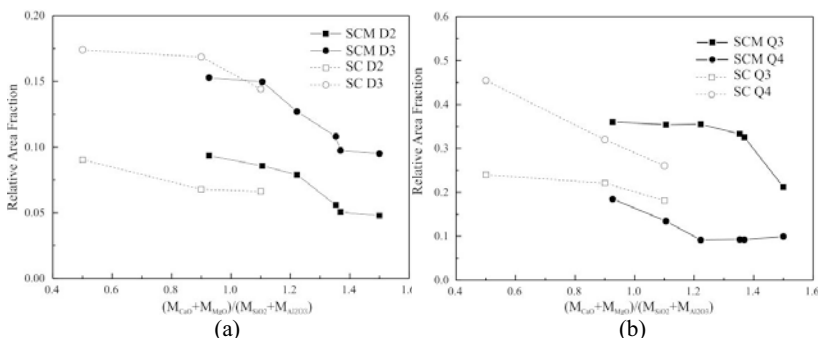
Figure 3. Abundance of structural units in the SiO₂-CaO system as a function of CaO/SiO₂ molar ratio

It is widely accepted that MgO performs as a network modifier similar to CaO [1]. At CaO/SiO₂ = 1, the Raman spectra of different MgO additions (5, 10, 15 and 20 mol%) are shown in Table IV. As the additions of MgO are increased from 5 to 20 mol%, the peaks D2 and D3 shift further from 635 to 658 cm⁻¹ and 680 to 697 cm⁻¹ respectively. However, the peaks Q1-Q4 do not have a clear shift trend with addition of MgO, which may be due to overlaps of the effects from Si-Ca and Si-Mg. From the area fraction trends, it still indicates the degradation of silicate network structure.

Table IV. Peak shift and relative area fraction of each peak in SiO₂-CaO-MgO Raman spectrum

CaO/SiO ₂	MgO mol%	D2	D3	Q1	Q2	Q3	Q4
Peak Shift							
1	5	635.3	680.1	860.7	903.2	965.0	1040.6
1	10	641.5	685.6	857.3	904.6	968.7	1061.4
1	15	655.1	696.2	853.1	895.4	960.8	1047.5
1	20	658.5	697.4	848.5	903.7	964.3	1026.4
Peak Area							
1	5	0.086	0.150	0.086	0.191	0.354	0.134
1	10	0.079	0.127	0.146	0.201	0.355	0.092
1	15	0.056	0.108	0.160	0.241	0.333	0.093
1	20	0.048	0.095	0.202	0.344	0.212	0.099

To further compare the depolymerization ability of CaO and MgO, the area of each peak is compared in the basicity ranges of 0.5 to 1.5. The molar ratio $(M_{CaO}+M_{MgO})/(M_{SiO_2}+M_{Al_2O_3})$ is used to describe the basicity in the present study. It can be seen from Figures 4 (a), (b) and (c), that the peaks D2, D3, Q3 and Q4 in both systems report a reducing trend with increasing basicity. In Figure 4c, the area fractions of peaks Q1 and Q2 increase with increasing basicity. In summary, within overlapping ranges of SiO₂-CaO and SiO₂-CaO-MgO systems, the comparisons report close area fractions in peak D2, D3 and Q1. The areas of peak Q2 and Q4 in the SiO₂-CaO system are larger than that in the SiO₂-CaO-MgO system. The degree of polymerization (DP) of two systems will be further discussed in the following section.



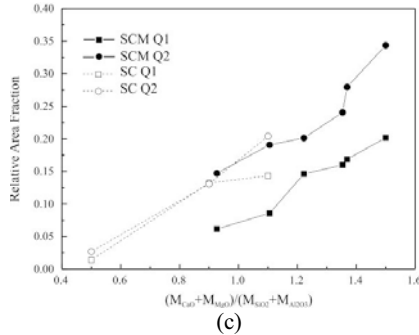


Figure 4: Area fraction of different peaks in the SiO₂-CaO and SiO₂-CaO-MgO systems as a function of basicity, (a) peak D2, D3; (b) peak Q3, Q4 and (c) peak Q1, Q2

The addition of Al₂O₃ was reported to enhance the polymerization of silicate melts [1]. Al₂O₃ will form [AlO₄]⁻ tetrahedral and connect with silicate network with charge balanced Ca²⁺. At CaO/SiO₂ = 1, Raman spectrum of the SiO₂-CaO-Al₂O₃ glass are presented in Table V.

Table V. Peak shift and relative area fraction of each peak in SiO₂-CaO-Al₂O₃ Raman spectrum

CaO/SiO ₂	Al ₂ O ₃ mol%	D2	D3	Q1	Q2	Q3	Q4
		Peak Shift					
1	5	570.7	679.9	864.1	895.2	945.8	1022.9
1	10	572.3	661.6	863.0	895.1	954.8	1037.9
1	15	551.8	657.2	874.7	913.4	966.3	1033.9
		Peak Area					
1	5	0.042	0.120	0.138	0.197	0.421	0.083
1	10	0.103	0.148	0.068	0.157	0.391	0.134
1	15	0.075	0.182	0.037	0.147	0.388	0.171

Due to the attachment of [AlO₄]⁻ unit onto silicate ring structure, the addition of Al₂O₃ shifts D2 and D3 peaks to the left, which indicates the increase of folded ring silicate structure. With the addition of Al₂O₃ content from 5 to 15 mol%, the area fractions of (Q1 + Q2) decrease, while the peak areas of (Q3 + Q4) increase. The tendencies of D2 and D3 assigned silicate ring structure are more complicated as the [AlO₄]⁻ may incorporate into silicate networks with charge compensated Ca²⁺.

Degree of polymerization

From Raman studies of the SiO₂-CaO, SiO₂-CaO-MgO and SiO₂-CaO-Al₂O₃ systems, the peaks can be classified into two groups. Peaks D2, D3, Q3 and Q4 are classified to be associated with polymerized silicate units, as their areas increase with increasing basicity. And peaks Q1 and Q2 are classified to be associated with depolymerized silicate units, because their areas decrease with increasing basicity.

In the present study, the area ratio of $(D2+D3+Q3+Q4)/(Q1+Q2)$ is used to represent the DP (degree of polymerization) index. The DP index is plotted against the basicity of the $\text{SiO}_2\text{-CaO}$, $\text{SiO}_2\text{-CaO-MgO}$ and $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$ systems. As shown in Figure 5, all three slag systems report decreasing trends while basicities increase. The degree of polymerization of the $\text{SiO}_2\text{-CaO}$ system is higher than that in the $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$ system at the same basicity, which may be due to the incorporation of the $[\text{AlO}_4]^-$ with Ca^{2+} in silicate network. At basicity 1.1, the substitution of Ca^{2+} by Mg^{2+} slightly increases the polymerization of silicate network.

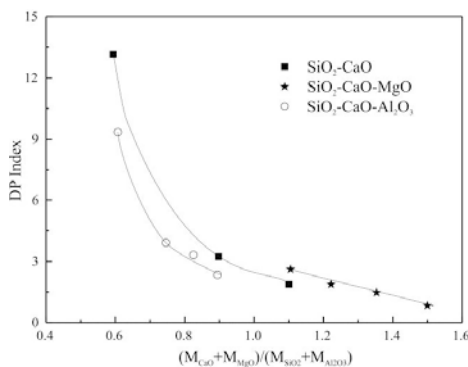


Figure 5. DP index agasin basicity for the $\text{SiO}_2\text{-CaO}$, $\text{SiO}_2\text{-CaO-MgO}$ and $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$ systems

Relationship with activation energies of slags

Arrhenius-type equation is widely used to determine the activation energy of slags. From the viscosity data in the $\text{SiO}_2\text{-CaO}$ [9], $\text{SiO}_2\text{-CaO-MgO}$ [10] and $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$ [11] systems, the activation energies can be determined and plotted against DP index. As shown in Figure 6, the activation energies clearly increase with increasing DP index. A polynomial equation can be drawn to describe the trend. Therefore, the DP index, which can be experimentally measured, can potentially be used to predict the activation energy of the silicate melts.

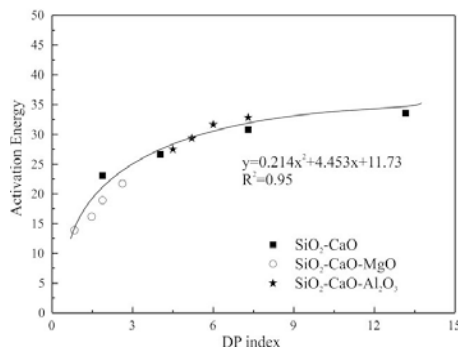


Figure 6. Correlation between activation energy and DP index of Raman spectrum

Conclusions

In the present study, the quenched slags in the SiO₂-CaO, SiO₂-CaO-MgO and SiO₂-CaO-Al₂O₃ systems were analyzed using Raman spectroscopy. The major bands located in 400-700 cm⁻¹ and 800-1200 cm⁻¹ were deconvoluted and assigned to folded rings and defect silicate units. It can be concluded that a high basicity will cause the bands at 400-700 cm⁻¹ shift to right and the bands at 800-1200 cm⁻¹ shift to left.

The peak areas of the Raman spectra can be quantitatively correlated to DP index. The DP index is proportional to the slag basicity and can be potentially used to predict the activation energy of the silicate melts.

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