

# Effect of the temperature on the structure of slag nanocrystalline glass-ceramics by Raman spectroscopy

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In the present paper, slag nanocrystalline glass-ceramic was produced by melting method. The slag nanocrystalline glass-ceramic was measured by Raman spectroscopy in the temperature range from -150 to 450°C, in order to study the effect of temperature on the structure of this system glass-ceramics. The results showed that different non-bridge oxygen bond silicon-oxygen tetrahedron structural unit changes are not consistent with rising temperature. Further analyses indicated that: the SiO<sub>4</sub> tetrahedron with 2 non-bridged oxygen (Q<sup>2</sup>), the SiO<sub>4</sub> tetrahedron with 3 non-bridged oxygen (Q<sup>1</sup>), which are situated at the edge of the 3-D SiO<sub>4</sub> tetrahedrons network, and the SiO<sub>4</sub> tetrahedron with 4 non-bridged oxygen (Q<sup>0</sup>), which is situated outside the 3-D network, they all have suffered a significant influence by the temperature change, which has been expressed as: shifts towards the high wave-number, increased bond force constants, and shortened bond lengths. This paper studied influence of temperature on slag nanocrystalline glass-ceramics using variable temperature Raman technology. It provides experiment basis to the research of external environment influence on slag nanocrystalline glass-ceramics materials in structure and performance. In addition, the research provides experimental basis for controlling the expansion coefficient of glass-ceramics.

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## 1. Introduction

Glass-ceramics offer the possibility of combining the special properties of conventional sintered ceramics with the distinctive characteristics of glasses [1]. Because of it has many unique properties, glass-ceramics is widely used in construction industry, electronic industry, biomedicine, optics, military domain. Therefore, many studies on the structure and properties of glass-ceramics have been a research focus in recent years, and some good results have been reported stress and corrosion of glass-ceramics [2-9]. As we all know, temperature is one of the most important factors in the application process. However, very little information is reported that temperature influence on the structure and properties of glass-ceramics.

In recent years, Raman spectroscopy has been employed to investigate the structure of glasses and ceramics [10]. Colombari [11] et al. summarized the structure of ceramic and glass unit and corresponding relationship between Raman spectral band and used the specific Raman parameters to analyze the composition of the ceramics and glass. However, there are few

researches into the structure of glass-ceramics with Raman spectroscopy [12,13]. This paper studies the influence of temperature on slag nanocrystalline glass-ceramics using variable temperature Raman technology. It provides experimental basis to the research of external environmental influence on slag nanocrystalline glass-ceramics materials in structure and properties.

## 2. Materials and methods

### 2.1 Materials

Glass-ceramic material was prepared from Bayan Obo tailing and fly ash as the main raw materials by the melting method. The chemical compositions of as-received Bayan Obo tailing and fly ash were listed in Table 1. Other pure chemical components as raw materials. Glass batches packing in corundum crucibles was melted in an electric furnace at 1470 °C for 4 h. The sample was nucleated at 720°C for 2h and then the glass sample was crystallized at 880°C for 2h.

Table 1. The chemical composition of the Bayan Obo tailing (BOT) and fly ash (wt.%).

Composition	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	FexOy*	BaO	MnO	Nb <sub>2</sub> O <sub>5</sub>	Cr <sub>2</sub> O <sub>3</sub>	CaF <sub>2</sub>	REO**	LOI***	Total
The BOT	27.56	7.20	20.23	5.32	0.50	1.84	19.84	2.28	1.36	0.20	0.05	10.35	1.25	2.02	100
Fly ash	51.68	30.70	3.89	0.76	1.62	1.84	7.43	-	-	-	-	-	-	2.08	100

\* FexOy: FeO and Fe<sub>2</sub>O<sub>3</sub>.

\*\* REO: rare earth oxides.

\*\*\* LOI: loss on ignition at 1000 °C.

## 2.2 Methods

The micro Raman spectrometer (Jobin Yvon, HR800) equipped with a 514.5-nm Ar<sup>+</sup> ion excitation laser (Spectra-Physics stabilite 2017) was used to obtain Raman spectra. The 50 objective was used for both laser illumination and Raman backscattering detection. Frequency calibration of the Raman spectrum was realized with the characteristic 520cm<sup>-1</sup> line of silicon and the resolution was 1 cm<sup>-1</sup>. The excitation power of 20 mW and exposure time (CCD integration times) of 10s were used to collect all Raman spectra.

The temperature controlling system is Linkam THMS G600 cooling bench, and the temperature changing rate is 5 °C min<sup>-1</sup>. The glass-ceramics samples we prepared were put in the sample pool, the temperature changes of the cooling bench were repeated for three times between -150 and 450 °C, to ensure the consistence of the actual temperature and the measured temperature in the sample pool.

## 3. Results and discussion

### 3.1 Raman spectrum of slag nanocrystalline glass-ceramics at room temperature

The Raman spectrum of slag nanocrystalline glass-ceramics at room temperature is shown in Fig. 1. It

can be observed that the Raman spectrum of slag nanocrystalline glass-ceramics, in the 400-850cm<sup>-1</sup> region, have three main bands. The Raman spectrum main bands at about 520 cm<sup>-1</sup>, 656 cm<sup>-1</sup>, 754 cm<sup>-1</sup> originate from the Q<sup>4</sup> units, from the Si-O-Si bending vibration and the Q<sup>0</sup> units, respectively [14]. The Raman spectrum in the region, 800-1200 cm<sup>-1</sup> presented in Fig. 1, shows one broad Raman bands. The bands have been assigned to the Si-O stretching in Q<sup>n</sup> species. Table 2 summarize the Raman peaks of slag nanocrystalline glass-ceramics.

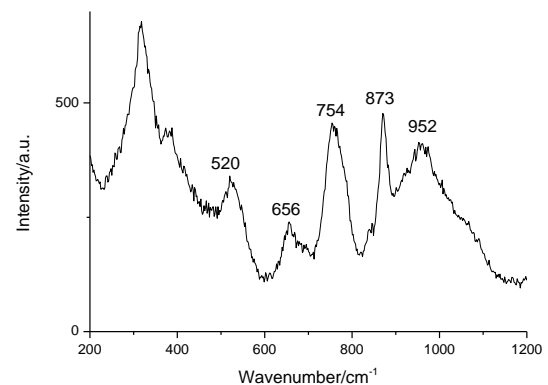


Fig. 1. Raman spectrum of slag nano-crystal glass-ceramics at room temperature.

Table 2. Assignment of slag nanocrystalline Glass-Ceramics Raman Peaks.

Raman band (cm <sup>-1</sup> )	Assignment of Raman bands
520 shoulder	Q <sup>4</sup>
656	Si-O-Si bending
754	Q <sup>0</sup>
800-1200	Si-O stretching vibration of Q <sup>n</sup> with different n (n=1,2,3,4)

### 3.2 Raman spectra of slag nanocrystalline glass-ceramics at different temperature

In order to simulate the most possible application temperature environment of glass-ceramic materials, we have measured the Raman spectra of slag nanocrystalline

glass-ceramics at temperature ranging from -150 to 450. Fig. 3 shows the Raman spectra of slag nanocrystalline glass ceramics for wave numbers between 200 and 1200 cm<sup>-1</sup> at a specific temperature range. Vibrations of Q<sup>4</sup> silica tetrahedra caused by the complete polymerization of the slag ceramic at ~520 cm<sup>-1</sup> exhibits no frequency

shift with temperature change. The Raman peak of symmetrical variable-angle vibrations of Si–O–Si at  $\sim 656\text{ cm}^{-1}$  is redshifted towards low wave numbers with increasing temperature. By contrast, the Raman peak of the Si–O stretching vibrations of  $Q^0$  is redshifted from  $763\text{ cm}^{-1}$  to  $739\text{ cm}^{-1}$  with increasing temperature. The redshifted Raman peak indicates that the force constant of Si–O bond in  $Q^0$  decreases and the bond length increases. Raman spectra of  $Q^n$  silica tetrahedra from  $800\text{ cm}^{-1}$  to  $1200\text{ cm}^{-1}$  are formed by the superposition of multiple Raman peaks. Spectral analysis reveals that temperature yields small effects on  $Q^4$  silica tetrahedron by complete polymerization of slag nanocrystalline glass ceramic, but significantly affects the structure of the symmetrical variable-angle vibrations of Si–O–Si. In addition, temperature yields the most significant effects on the Si–O stretching vibration of  $Q^0$ . These results differ from the Raman spectra of pure glass ceramics in previous studies. The symmetrical variable-angle vibrations of Si–O–Si vary in the entire temperature range in contrast to that of the Raman spectra in previous studies because of the effects of rare earth and other microelements in slag nanocrystalline glass ceramics on the structure.

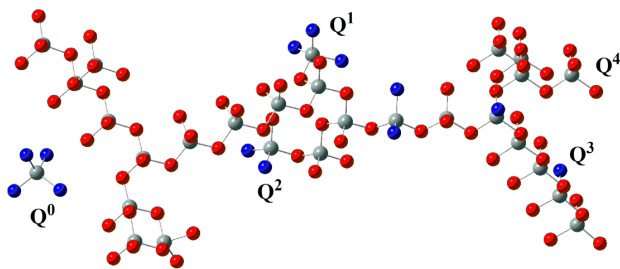


Fig. 2. Schematic diagram of the different  $SiO_4$  tetrahedral structure units: isolated ( $Q_0$ ), connected with one ( $Q_1$ ), two ( $Q_2$ ), three ( $Q_3$ ), and four ( $Q_4$ ) Si–O–Si bridge tetrahedral are indicated [15].

Fig. 3 shows the multi-peak fitting spectrograms of the Raman spectra of  $Q^n$  silica tetrahedra from  $800\text{ cm}^{-1}$  to  $1200\text{ cm}^{-1}$  for slag nanocrystalline glass ceramics. The wave number range represents the Raman spectra of Si–O stretching vibrations of  $Q^1$  silica tetrahedron with three non-bridging oxygen bonds at  $\sim 875\text{ cm}^{-1}$ , Si–O stretching vibrations of  $Q^2$  silica tetrahedron with two non-bridging oxygen bonds at  $\sim 920\text{ cm}^{-1}$ , Si–O stretching vibrations of  $Q^3$  silica tetrahedron with one non-bridging oxygen bond at  $\sim 960\text{ cm}^{-1}$ , and Si–O stretching vibrations of  $Q^4$  silica tetrahedron with one non-bridging oxygen bond at  $\sim 1010\text{ cm}^{-1}$ . Multi-peak fitting results on the Raman spectra of  $Q^n$  silica tetrahedra for slag nanocrystalline glass ceramics are in agreement with those from the theoretical analysis of Colombari et al [11].

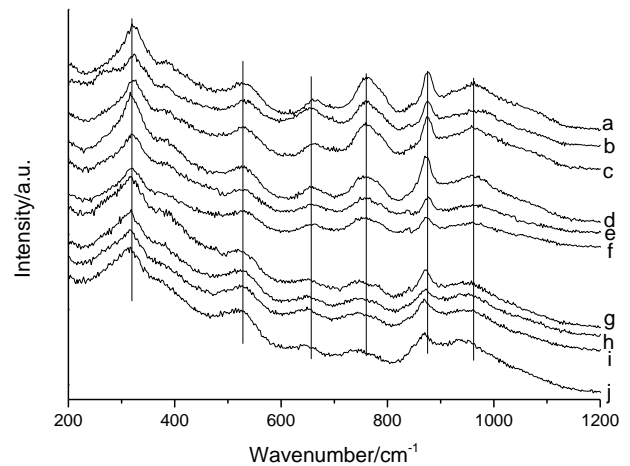


Fig. 3. Raman spectra of slag nanocrystalline glass-ceramics at different temperature (a:  $-150$ , b:  $-100$ , c:  $-50$ , d:  $0$ , e:  $50$ , f:  $150$ , g:  $200$ , h:  $300$ , i:  $400$ , j:  $450$ ).

Table 3 shows the change rules of Raman spectra of slag nanocrystalline glass ceramics from  $500\text{ cm}^{-1}$  to  $1200\text{ cm}^{-1}$  with temperature. Si–O stretching vibrations of  $Q^4$  and  $Q^2$  exhibit no marked shifts under temperature effects. However, vibrations of approximately three wave numbers are observed compared with those of other Raman peaks that shift at several wave numbers. All the analyzed Raman peaks shift towards low wave numbers with increasing temperature. These results imply that the force constant of the bonds decreases and the bond length increases with increasing temperature for the Raman bands of slag nanocrystalline glass ceramics. These values indicate that in the 3D network structure of silica, the structural unit of  $Q^4$  in the center is the least affected by temperature, followed by those of  $Q^1$  and  $Q^2$  at the edges. The structural unit of  $Q^3$  near the center is relatively affected, whereas that of  $Q^0$  outside the silica structure is the most significantly affected. Furthermore, all Raman peaks from  $-50\text{ }^\circ\text{C}$  to  $150\text{ }^\circ\text{C}$  exhibit small shifts. Si–O stretching vibrations of  $Q^0$  exhibit the highest shift of a few wave numbers, which indicate that slag nanocrystalline glass ceramics are often unaffected by temperature in normal-temperature environments. The results further reveal that the effective control of  $Q^0$ ,  $Q^3$ , and  $Q^2$  generation in the preparation of slag nanocrystalline glass ceramics yields microcrystalline glass materials with low expansion coefficients.

Table 3. Raman bands of slag nanocrystalline glass ceramics at different temperature.

T/°C	Q <sup>1</sup>	Si-O-Si	Q <sup>0</sup>	Q <sup>1</sup>	Q <sup>2</sup>	Q <sup>3</sup>	Q <sup>4</sup>
-150	527	663	763	876	911	961	1010
-100	527	657	759	876	911	961	1010
-50	527	657	759	876	911	961	1010
0	525	655	754	874	909	959	1009
50	525	655	752	874	907	959	1009
100	525	655	752	874	907	959	1009
150	525	655	752	874	907	959	1009
200	525	652	747	872	906	957	1008
250	525	650	745	872	904	956	1008
300	523	648	743	872	902	954	1008
350	523	648	741	870	900	949	1006
400	523	646	741	870	899	945	1006
450	523	643	739	870	899	940	1006

#### 4. Conclusion

This paper studies the influence of temperature on the structure of slag nanocrystalline glass-ceramics using variable temperature Raman technology. The result shows that between -150°C and 450 °C, the influence of the temperature on the structure units of the three-dimensional SiO<sub>4</sub> tetrahedrons network in slag nanocrystalline glass-ceramics is more and more noticeable from the center to the edge, the concrete degree of influence order Q<sup>3</sup>>Q<sup>0</sup>>Q<sup>2</sup>>Q<sup>1</sup>>Q<sup>4</sup>. This paper also provides a new experimental method to the research on the structure and preparation of slag nanocrystalline glass-ceramic.

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