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## The influence of $\text{Na}_2\text{O}$ on the fast diffusion layer around diopside crystals

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The establishment of a fast diffusion layer in glass-ceramics can reduce carbon emissions and manufacturing cost during their preparation. In this study a  $\text{CaO}-\text{MgO}-\text{SiO}_2$  (CMS) glass-ceramic was prepared by forming a fast diffusion layer doped with different  $\text{Na}^+$  contents, taking advantage of differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and energy dispersive spectroscopy line scanning (EDSLS). Upon increasing the  $\text{Na}^+$  content from 0.10 mol to 0.14 mol, the number of crystal particles increased by 350%. The  $\text{Na}^+$  content in the fast diffusion layer around the crystal particles decreased, which ultimately affected the crystal growth. This result may benefit the fast diffusion layer theory on the inhibitory effect of Na during crystal growth.

### 1. Introduction

Glass-ceramics combine crystalline and amorphous features,<sup>1,2</sup> and are produced by melting the parent glass, followed by a heat treatment step. By adjusting the composition and regulating the heat treatment process, the properties of the glass-ceramic can be controlled,<sup>3,4</sup> such as mechanical strength, chemical resistance and abrasive resistance.<sup>5,6</sup> Glass-ceramics have been widely used in several fields, particularly with respect to applications in solid oxide fuel cells, optics, photonics, biomedicine materials and construction materials.<sup>7–11</sup>

Usually, the production of glass-ceramics requires two heat treatment steps (nucleation and crystal growth) due to its poor crystallization ability. However, the two heat treatment steps consume a lot of energy and emit a large amount of carbon. Hence, improving the parent glass' nucleation and crystal growth capacities is a way of reducing the energy consumption and carbon emissions.

Recently, numerous studies on glass-ceramics have focused on the nucleation and crystal growth steps, which are related to the diffusion layer around the crystals.<sup>12–15</sup> In multi-component systems, doping with small amounts of other components affects the crystal growth.<sup>2</sup> Generally, during the crystallization of the glass-ceramic, both a nucleating agent and network modifiers are concentrated in the crystal nuclei. Moreover, the glass network formers (Al, Si) are concentrated on the glass layer between the residual glass and the crystal.<sup>16</sup> Eventually, the glass layer limits the diffusion of ions in the crystal phase like

$\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . Wisniewski and co-authors<sup>17</sup> described the crystallization process in which the formation of concentration gradients decelerates the crystal growth. This phenomenon leads to an increase in the viscosity of the diffusion layer and results in a smaller diffusion rate, which ultimately affects the crystal growth. In Yang's study, the melts contained an excess of alkali metal ions.<sup>18</sup> During crystallization, the excess alkali metal ions lead to increasing amounts of Si–O–Na bonds in the residual glass phase, which result in an increase in the diffusion coefficients and the formation of a fast diffusion layer.

However, most studies have focused on the formation of the diffusion limiting layers during the crystallization process.<sup>19,20</sup> Yang and co-authors described a phenomenon in which the diffusion limiting layers become a fast diffusion layer.<sup>18</sup> By adding excess  $\text{Na}_2\text{O}$  and  $\text{CaF}_2$ , a fast diffusion layer was formed around the crystals to help increase the diffusion coefficient of the crystal phase ions. Thus, the crystal growth was accelerated. Nevertheless, studies on the effect of the  $\text{Na}^+$  content in the diffusion layer are rarely reported.<sup>18</sup>

In this study, an excess of  $\text{Na}_2\text{O}$  was added in the CMS system. During crystallization,  $\text{Na}^+$  was considered as a glass modifier, which forms the diffusion layer. The crystallization kinetics index of the glass-ceramics was calculated using the Kissinger and Augis–Bennett equations. The results indicated that an excess of  $\text{Na}^+$  inhibits the crystal growth. The study presented herein directly tests the fast diffusion layer theory.

### 2. Experimental

The parent glass was prepared from the highly purified raw materials  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{CaF}_2$  and  $\text{Na}_2\text{CO}_3$  (purity 99%; China Medicine, Inc.). Prior to use,  $\text{CaO}$  and  $\text{Na}_2\text{CO}_3$  were heated at 900 °C for 2 h. The thermal

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Table 1 The chemical compositions (g) of the raw materials

Sample	CaO	MgO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	CaF <sub>2</sub>	Na <sub>2</sub> O
GC-1	20.1	13.3	46.6	4.4	5.3	1.2	7.9	0
GC-2	20.1	13.3	46.6	4.4	5.3	1.2	7.9	7.4 (0.12 mol)
GC-3	20.1	13.3	46.6	4.4	5.3	1.2	7.9	8.7 (0.14 mol)

decomposition of CaO removed impurities such as CaCO<sub>3</sub> and Ca(OH)<sub>2</sub>. Na<sub>2</sub>O was obtained *via* the decomposition of Na<sub>2</sub>CO<sub>3</sub>.

A batch of raw materials was homogeneously mixed for 1 h in a ball mill. The mixed raw materials were packed in a corundum crucible and melted at 1450 °C for 2 h for complete melting and homogenization. The melt was quenched into a preheated iron mold (600 °C) for 30 min in order to remove the internal stress. Then, the parent glass was cut into small pieces. The glass-ceramic samples were obtained by annealing the parent glass pieces. The heat treatments were carried out at the temperatures around the  $T_p$  for 20 min, 30 min and 60 min, respectively. The glass compositions are given in Table 1.

Thermal analysis was performed using differential scanning calorimetry (DSC, NETZSCH STA 409C/CD) with the powdered parent glass sample (quenched into water) at heating rates of 10 °C min<sup>-1</sup>, 15 °C min<sup>-1</sup>, 20 °C min<sup>-1</sup> and 25 °C min<sup>-1</sup> from room temperature to 1000 °C. The glass crystallization temperatures ( $T_p$ ) at the different heating rates were obtained from these measurements. After heating at the  $T_p$ , the glass ceramics were obtained.

The diffraction patterns of the glass-ceramics were obtained *via* X-ray diffraction (Philips APD-10, monochromatic Cu K $\alpha$  radiation). The Fourier transform infrared (FTIR) spectra of the glass-ceramics were taken on Nicolet-is 10 spectrophotometer in the range of 400–4000 cm<sup>-1</sup>. KBr was mixed with the sample powders and palletized using a hydraulic press. The contribution of KBr was cancelled out by normalizing the spectrum of each sample to the spectrum of KBr. High resolution scanning electron microscopy (SEM) images of the glass-ceramic samples were recorded on Carl Zeiss EVO 18. The fractured surface was etched with diluted HF (5%) to prepare the samples for SEM.

### 3. Results and discussion

Fig. 1(a) and (b) show the DSC curves obtained for the parent glass powder at different heating rates. In Fig. 1(a), one crystallization exothermic peak was observed in the DSC curves at the heating rates of 10 K min<sup>-1</sup>, 15 K min<sup>-1</sup>, 20 K min<sup>-1</sup> and 25 K min<sup>-1</sup>. The DSC curves showed the crystallization temperature ( $T_p$ ) ranging from 1119.3 K to 1148.3 K. The crystallization exothermic peak temperature increased as the heating rate increased. Basically, as the heating rate slowed down, diffusion and atomic rearrangements transformed the structure from non-crystalline to crystalline. When the crystalline phase transformation rate was very slow, the crystallization exothermic peak of the glass was flat. However, as the heating rate increased, the crystallization of the glass transition was faster. The transformation rate increased upon increasing the crystallization temperature and the crystallization exothermic peak became sharp.

Nucleation shows endothermic effects, while crystallization shows exothermic effects. The endothermic and exothermic peaks in the DSC curves were due to nucleation and crystallization, respectively. The crystallization temperature depends on the exothermic temperature due to the increasing crystallization rate. When compared to GC-2 and GC-3, the increase in sodium content significantly reduces the  $T_p$ , indicating that Na<sup>+</sup> accelerates the crystallization of the glass.

The kinetic parameters, such as the crystallization activation energy, depend on the obtained DSC curves. The Kissinger equation can be used to assess the crystallization dynamics:<sup>21</sup>

$$\ln \frac{\alpha}{T_p^2} = -\frac{E_a}{RT_p} + C \quad (1)$$

herein,  $\alpha$  is the DSC heating rate,  $E_a$  is the crystallization activation energy,  $T_p$  is the crystallization exothermic peak temperature and  $R$  is the gas constant. The plot of  $\ln(\alpha/T_p^2)$  versus  $1000/T_p$  is shown in Fig. 1 and the activation energy  $E_a$  was calculated from the slope of the plot. The crystal growth index  $n$  was calculated from the Augis-Bennett equation:

$$n = \frac{2.5}{\Delta T} \frac{RT_p^2}{E_a} \quad (2)$$

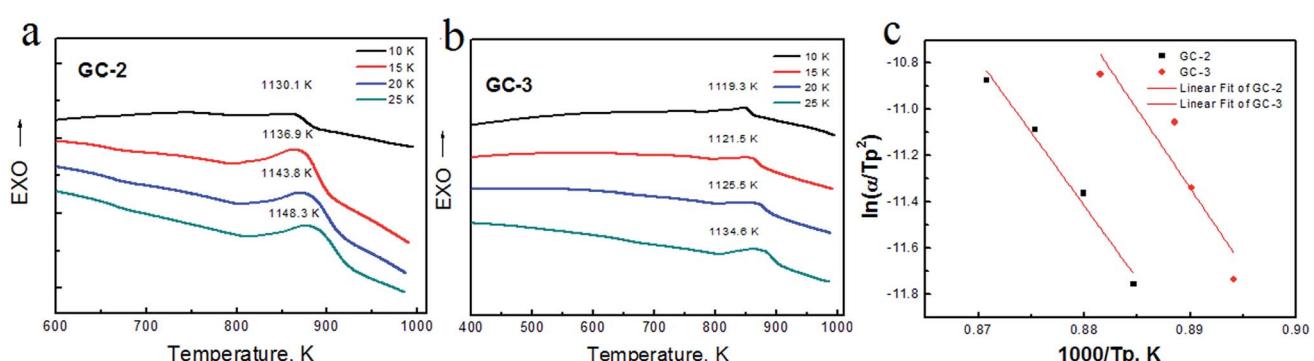


Fig. 1 (a) The DSC curves obtained at 10 K min<sup>-1</sup>, 15 K min<sup>-1</sup>, 20 K min<sup>-1</sup> and 25 K min<sup>-1</sup> for GC-2, (b) the DSC curves obtained at 10 K min<sup>-1</sup>, 15 K min<sup>-1</sup>, 20 K min<sup>-1</sup> and 25 K min<sup>-1</sup> for GC-3 and (c) the variation of  $\ln(\alpha/T_p^2)$  1000/T<sub>p</sub> for the different CMS glasses.



herein,  $\Delta T$  is the full width at half maximum of the exothermic peak intensity. The corresponding crystallization activation energy ( $E_a$ ), the crystal growth index  $n$  and coefficients of determination ( $R^2$ ) are summarized in Table 2. The correlation between the Avrami index  $n$  and the crystallization mechanism of the glass is:  $n = 1$  is surface crystallization, while  $n \geq 3$  implies three dimensional crystallization.

Fig. 2 shows the XRD patterns of the samples heat-treated at the crystallization peak temperatures for 1 h. To confirm the nature of the obtained materials, X-ray diffraction studies were carried out. As seen in Fig. 2, the broad scattering peak in GC-1 suggests that no crystals precipitated in the glass matrix. The major phase of GC-2 and GC-3 was diopside, indicating that the addition of  $\text{Na}_2\text{O}$  has no effect on the main crystalline phase. The secondary phase of GC-2 was nepheline. With the addition of  $\text{Na}_2\text{O}$ , the secondary phase transferred to sodium aluminosilicate ( $\text{Na}_6\text{Al}_4\text{Si}_4\text{O}_{17}$ , 76-2385#) in GC-3. This indicates that at the end of the crystallization process,  $\text{Na}^+$  was rich in the residual glass. The nepheline and sodium aluminosilicate phases were formed by these  $\text{Na}^+$  ions, silicon and aluminum.

In order to characterize the structural building units of the glass ceramics, infrared absorption measurement studies were performed on the glass ceramics. Fig. 3 presents the FT-IR spectra of the glass ceramics with different  $\text{Na}^+$  contents. As seen in the spectra, there were characteristic absorption bands ranging from 400 to  $1200\text{ cm}^{-1}$ , which were due to the main silicate network group vibrations with different bonding arrangements. The absorption band about  $450\text{ cm}^{-1}$  was attributed to the bending vibrations of the  $\text{Al}-\text{O}-\text{Al}$  or  $\text{Al}-\text{O}-\text{Si}$  bonds.<sup>22</sup> The absorption band located at about  $490\text{ cm}^{-1}$  was associated with the  $\text{Si}-\text{O}-\text{Si}$  bending vibration mode. The broadened band at  $750\text{ cm}^{-1}$  indicates the scission of the  $\text{Si}-\text{O}-\text{Si}$  chain in the glass network.<sup>23</sup> The band located at about  $940\text{ cm}^{-1}$  was assigned to  $\text{Si}-\text{O}$  with two non-bridging oxygens.<sup>24</sup> The band located at about  $1040\text{ cm}^{-1}$  is characteristic of the

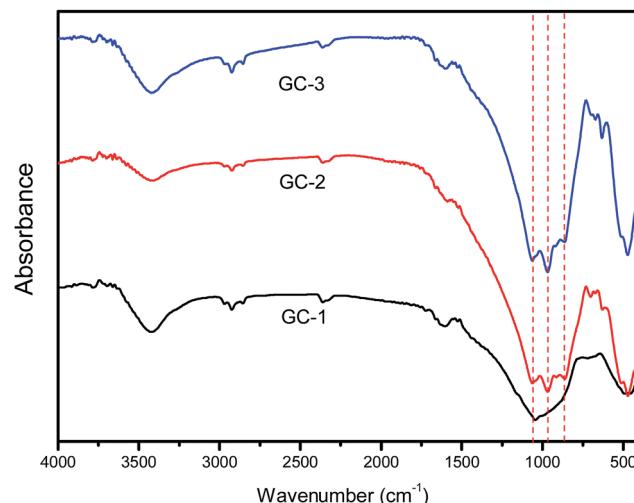


Fig. 3 The FT-IR absorption spectra of the prepared glasses.

asymmetric stretching vibrations of  $\text{Si}-\text{O}-\text{Si}$  bonds with a three-dimensional network structure. Upon the addition of  $\text{Na}^+$ , the  $\text{Si}-\text{O}-\text{Si}$  chain and non-bridging oxygens evidently increased. This led to a decrease in the integrity of the glass network.

The microstructures of the fractured surfaces of the glass ceramics prepared using different amounts of  $\text{Na}_2\text{O}$  are shown in Fig. 4. GC-1 was heat-treated at  $1120\text{ K}$  for 1 h and is shown in Fig. 4(a). No crystalline phase appears in the annealed glass, which may be due to the lack of  $\text{Na}_2\text{O}$ . Fig. 4(b) and (c) display the GC-2 sample heat-treated at the targeted temperature for 20 min and 30 min. The addition of  $\text{Na}_2\text{O}$  leads to crystal particles being formed in the glass ceramics. The black matrix is the glassy phase, which does not tend to crystallize further. Fig. 4(b) displays diopside crystals (very light grey) and the residual glassy phase (black). With the heat treatment time extended to 30 min, the crystal particles in the glass ceramics are apparently grown further. A similar microstructure was also evident for the GC-3 sample containing  $0.14\text{ mol Na}^+$ . Fig. 4(d)–(f) display the GC-3 sample heated for 5 min, 20 min and 30 min, respectively. According to Fig. 4(d), the addition of  $0.14\text{ mol Na}^+$  results in small crystal particles formed in 5 min. Extending the heat treatment time lead to the continuously growth of the crystal particles, while the crystallite dimensions were evidently smaller than those of GC-2. In addition, the number of crystal particles in the field of view in GC-3 was significantly higher. Thus, it is reasonable to say that the addition of  $\text{Na}_2\text{O}$  contributes to the crystal particles refinement and improves the crystal nucleus density.

Evaluation of the chemical composition of the glass-ceramics interface was performed *via* SEM and the energy dispersive X-ray spectroscopy (EDXS) line scan. Fig. 5(a) shows the micrograph of GC-3 and the EDXS line scan up the trace of the straight line shown in the micrograph. The distribution of sodium, magnesium and oxygen differs between the crystal particle and the residual glass phase. The  $\text{Na}^+$  content in the crystal particle is significantly lower than that in the residual glass. The  $\text{Mg}^{2+}$  and  $\text{O}^{2-}$  ion contents in the crystal particle are higher than that in the residual glass. This phenomenon means

Table 2 The crystallization activation energy  $E_a$ , crystal growth index  $n$  values and coefficients of determination for the different  $T_p$

	$E_a, \text{ kJ mol}^{-1}$	$n$	$R^2$
$T_{p1}$	498	6.0	0.97299
$T_{p2}$	567	5.2	0.81175

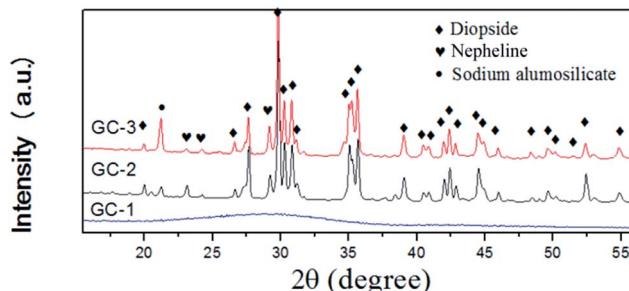


Fig. 2 The XRD patterns of the prepared glasses.



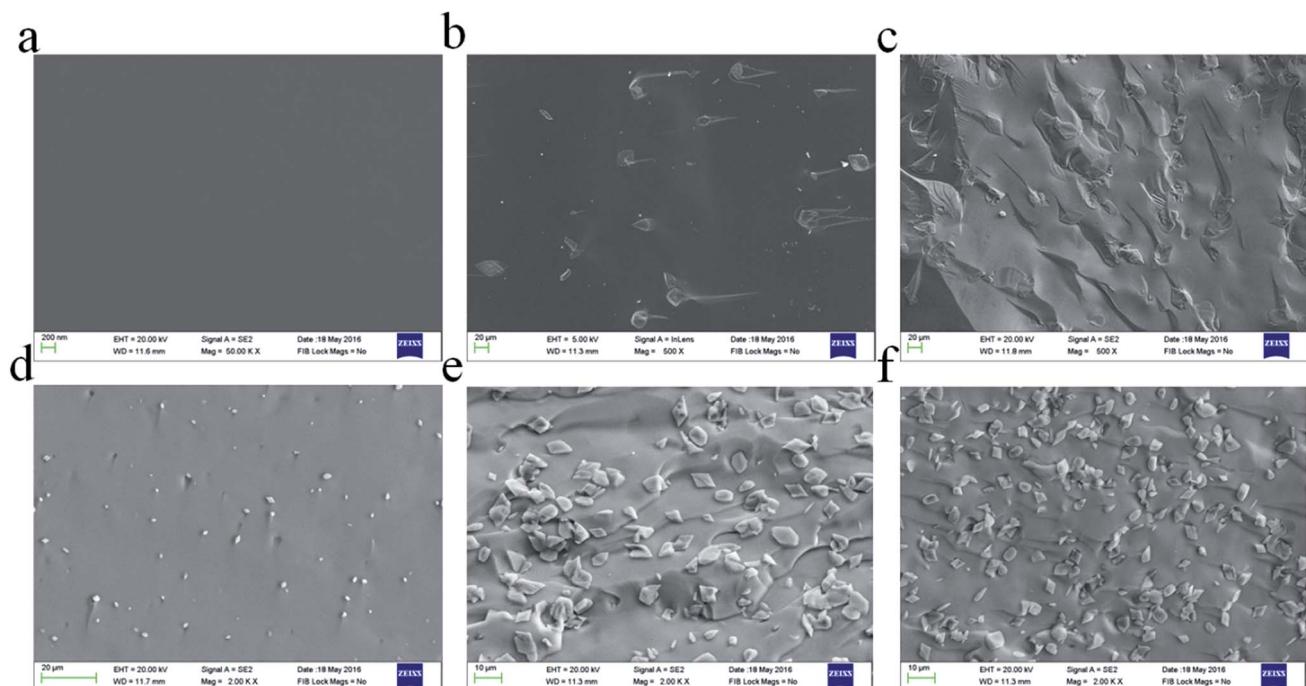


Fig. 4 (a) GC-1;  $\text{Na}^+$  0 mol, (b) GC-2;  $\text{Na}^+$  0.10 mol (heated at 1119 K for 20 min), (c) GC-2;  $\text{Na}^+$  0.14 mol (heated at 1119 K for 30 min), (d) GC-3;  $\text{Na}^+$  0.14 mol (heated at 1130 K for 5 min), (e) GC-3;  $\text{Na}^+$  0.14 mol (heated at 1130 K for 20 min) and (f) GC-3;  $\text{Na}^+$  0.14 mol (heated at 1130 K for 30 min).

that the  $\text{Na}^+$  ions diffused into the glass layer around the crystal during the crystallization process. While this process proceeds, the diffusion of  $\text{Mg}^{2+}$  and  $\text{O}^{2-}$  to the crystal nucleus occurs at the same time.

During the crystallization process, the phase separation, nucleation and crystal growth take place at the same time at the  $T_p$ . In general, the amorphous glass will be divided into the residual glass phase and the phase-separated regions during the phase separation stage. The enriched elements in the phase separation region are similar to the resulting crystal nucleus. Thus, the formation of a crystal nucleus is easier. During the crystallization of the CMS glass-ceramics, the addition of Na leads to an increase in the number of  $\text{Si}-\text{O}-\text{Na}$  bonds and non-bridging oxygen atoms. This further promotes the diffusion of calcium ions and magnesium ions, thereby promoting the crystal growth. As a result, the nucleation activation energy is decreased.

In a previous study,<sup>18</sup> the activation energy of CMS glass ceramics with 0 mol  $\text{Na}^+$  was found to be 301.2  $\text{kJ mol}^{-1}$ . The activation energy of the 0.1 mol  $\text{Na}^+$  added sample was 195.4  $\text{kJ mol}^{-1}$ . In this study, the activation energy after the addition of 0.12 mol  $\text{Na}^+$  was 498  $\text{kJ mol}^{-1}$  and after the addition of 0.14 mol  $\text{Na}^+$  it was 567  $\text{kJ mol}^{-1}$ . A high activation energy value means that the nucleation and crystallization was difficult. The activation energy decreased with  $\text{Na}^+$  ranging from 0 mol to 0.1 mol. The activation energy increased with  $\text{Na}^+$  ranging from 0.12 mol to 0.14 mol. In brief, different sodium ion contents (0 mol, 0.1 mol, 0.12 mol and 0.14 mol) have a non-linear relationship with the activation energy of the CMS glass-ceramics.

FT-IR spectra showed that the addition of sodium ions affects the glass network (Fig. 3). The addition of sodium ions produces a large number of non-bridging oxygen atoms. This phenomenon was consistent with the sodium ions acting as a network former that influences the glass network. At the same time, it can be found that excessive sodium ions (0.14 mol) do not affect the new structures generated in the glass network. The XRD patterns showed that the main phase did not change upon increasing the sodium ion content.

The sodium layer was found between the nuclei and residual glass. The results of EDX-line scanning performed on the GC-2 and GC-3 samples show that the  $\text{Na}^+$  content around the crystals was gradually changed. This also means that the glass network integrity around the nuclei was different. This phenomenon affects the diffusion rate. During the growth of the nuclei, the diffusion of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  occurs through the sodium ion layer around the crystal nuclei. When the sodium layer changes, it may have an effect on the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  diffusion velocity.

By means of the SEM micrographs shown in Fig. 4, it can be seen that the increase in sodium ion content results in an increase in the crystal number. As shown in Fig. 4(b) and (e), the number of crystal particles in the same area by counting was 68 and 239 (increased by 350%), respectively. This might be assumed as a result of sodium ions increasing the nucleation density during the isothermal hold. In GC-3, the non-bridging oxygen makes the glass network open. Therefore, the crystal nucleus is easier to generate. This phenomenon leads to a decrease in the sodium ion content around the crystal nucleus, thereby reducing the diffusion rate of the calcium ions. When the nucleation ends, the relative lack of sodium ions



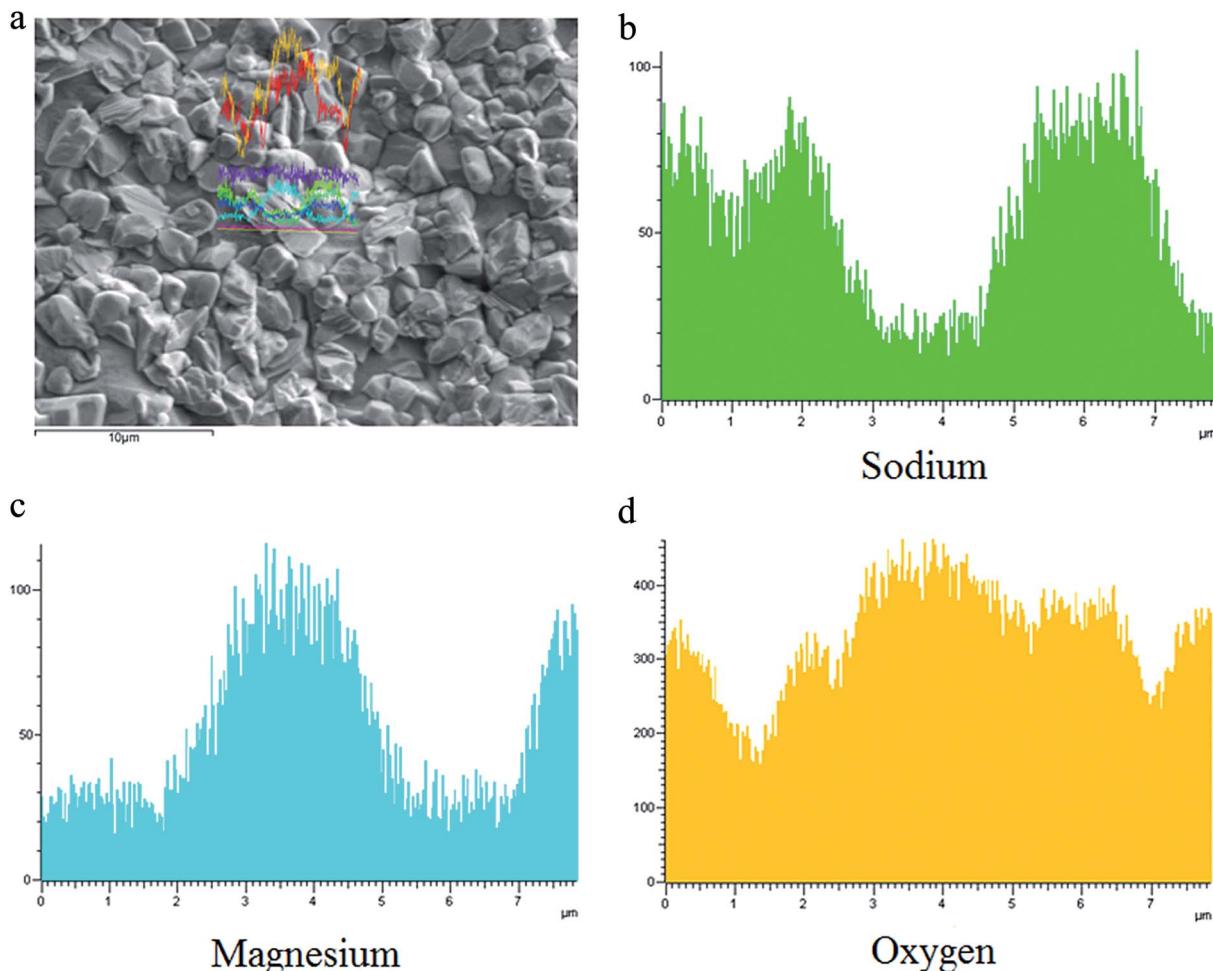


Fig. 5 (a) A micrograph of the GC-3 sample heated at 1119 K for 60 min and EDXS line scanning along the trace of the straight line indicated in the micrograph. (b) The sodium ion content obtained via the EDXS line scan of GC-3; (c) the magnesium ion content obtained via the EDXS line scan of GC-3 and (d) the oxygen ion content obtained via the EDXS line scan of GC-3.

formed around the crystal nucleus leads the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  diffusion mobility to decrease.  $E_a$  reflects the crystallization process. A comparison of the crystal nuclei growth can also verify the abovementioned assumptions. During the first 5 minutes of the isothermal process at  $T_p$ , the crystals grow in GC-3 first. This phenomenon proves that an excess of Na improves the nucleation ability. However, the size of the crystal nuclei in GC-3 is smaller than that in GC-2, which is obtained from the isothermal heat treatment for 20 minutes. This phenomenon proves that the lack of sodium content around the crystal nuclei inhibits the crystal growth. The abovementioned evidence shows that the sodium ions make the crystallization process easier but limit the nuclei crystals' continued growth. In summary, the excessive sodium ion content makes the activation energy increase abnormally.

## 4. Conclusion

In this study, the CMS glass-ceramic was prepared *via* a one-step heat treatment process, during which a fast diffusion layer was formed. During the crystallization process,

diopside crystals phase out of the homogeneous parent glass and concomitantly form a glass layer between the diopside and residual glass. As observed experimentally, the addition of sodium ions promoted the formation of Si-O-Na bonds. The Si-O-Na bonds in the glass layer will lead to an increase in the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  diffusion mobility and further promotes the formation of diopside. Upon increasing the  $\text{Na}^+$  content from 0.10 mol to 0.14 mol, the number of crystal particles increased 3.5 fold. The  $\text{Na}^+$  content in the fast diffusion layer around the crystal particles decreased. This phenomenon lead to the number of Si-O-Na bonds around the crystal nucleus to decrease, thereby inhibit the crystal growth.

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