Analysis of Reaction Crystallization Process of Wollastonite Glass Ceramics Using Infrared Spectra

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Abstract. The wollastonite glass ceramics were successfully prepared using waste glass and gehlenite powder. The effects of preparation process parameters on synthesis of wollastonite glass ceramics were studied by fourier transform infrared spectoscopy (FT-IR). The crystalline phase, crystal morphology of wollastonite glass ceramics were characterized by XRD and SEM. The results show that the flake like wollastonite glass ceramics can be obtained by changing the sintering temperature, the content of gehlenite and the holding time when using the reaction crystallization method. With the increasing of each preparation condition parameter, the increase of [Si-O] unsaturated degree will aggravate the fracture of network structure and then lead to various network fractures. The optimum preparation conditions were confirmed as follows: sintering temperature of 900 ºC, content of gehlenite of 30 %, holding time of 2 hours.

1. Introduction

Glass ceramics is a kind of material which is made of glass and ceramics. Owing to its properties of high changeable thermal expansion, very good thermal shock resistance, high mechanical strength, low dielectric loss and nice electrical insulation, it has been widely used in broad area\cite{1-3}.

Silicate glass ceramics are mainly composed of silicate crystal phases of alkali metal and alkaline earth metal, so the properties of these crystal phases determine the properties of the prepared glass ceramics to a certain extent. Silicate glass ceramics can be roughly divided into: enstatite (MgSiO\textsubscript{3}), wollastonite (CaSiO\textsubscript{3}) and lithium silicate (Li\textsubscript{2}SiO\textsubscript{3}, Li\textsubscript{2}Si\textsubscript{2}O\textsubscript{5})\cite{4}. As a kind of silicate glass ceramics, wollastonite glass ceramic have the advantages of high strength, beautiful color and no radioactivity, which is a new type of building decoration material instead of natural stone. Wollastonite glass ceramics are widely used in building ceramics, coatings, plastics, metallurgy, refractories and other sectors, and obtained in-depth research\cite{5-7}.

The traditional preparation process of glass ceramics is melting method. The melting temperature of glass is high, the production process is complex and the production cost is high. The technological process of preparing glass ceramics by sintering method is as follows: batching melting, water quenching, grinding, forming and sintering. It makes use of the nucleation on the surface of the glass powder, so that the sintering and crystallization can be completed at one time. The main advantages of sintered glass ceramics are fine particles, increased surface area, no need of nucleating agent, and easier crystallization than melting. The sintering method can overcome the shortcomings of the melting method, such as limited melting temperature and long heat treatment time. In addition, the preparation of glass ceramics by sintering does not need to go through the stage of glass formation, so
it can be used for the preparation of glass ceramics with high temperature requirements and high technical requirements. This method provides a new way for the preparation of new glass ceramic materials.

At present, many researches are focused on sintered glass ceramics of cordierite, enstatite and Al-Si system, such as porous glass ceramics, low temperature sintered glass ceramic substrate with main crystal phase of chrysocolla, which is the main production process of new high-grade building decoration materials.

Reactive crystallization sintering method is a patented technology for the preparation of glass ceramics from waste glass. It can directly add crystallization promoters to waste glass for sintering, which can greatly reduce production costs and realize resource recycling. Reaction crystallization sintering method directly adds the synthesized crystallization promoter to the glass powder for sintering and has simpler operation and lower cost than sintering method, thus obtaining glass ceramics[8-10]. In this study, wollastonite glass ceramics were prepared use gehlenite as the promoter. The effects of preparation process parameters on synthesis of wollastonite glass ceramics were studied by FT-IR. The wollastonite glass ceramics prepared under optimum preparation conditions were characterized.

2. Experimental
Preparation of glass powder. Clean the collected waste glass, smash it with an iron bar, smash it to particles, pass a 30 mesh sieve, put the screened glass particles into the grinding tank, take out the glass powder, and select a sufficient 120 mesh glass powder for standby.

Preparation of wollastonite glass ceramics. The waste glass powder mixed with 10%, 20%, 30%, 40% and 50% gehlenite powder (size of 180 mesh) by weight, respectively. The PVA water solution (6%) as a binder was added to the mixed powder, after that press mixed powder into a cylindrical compacts at 7.5 Mpa (ϕ 13 mm × 5 mm). The cylindrical compacts were sintered with temperature of 800~1000 ºC for 2 h and holding time with 0.5~4h.

Characterization of wollastonite glass ceramics. Reaction crystallization process of wollastonite glass ceramics was characterized by FT-IR. The crystalline phase of the glass ceramics was characterized by x-ray diffraction (XRD, Empyrean) with Cu Ka radiation. The morphology of the glass ceramics were observed by scanning electron microscopy (SEM, JSM-6360LV).

3. Results and Discussion
The FT-IR spectra of the glass ceramics with different calcination temperature were displayed in Fig. 1. From the Fig. 1, the FT-IR spectra of the sample not calcined shows five main absorption bands, the band near 480 cm−1 could be assigned to the bending vibration of Si-O-Si linkages. The band located at 676 cm−1 could be attributed to symmetric stretching vibration of Si-O-Si bond and the absorption peak near 785 cm−1 belongs to bending vibration of Al-O-Al in [AlO4] or symmetric stretching vibration of Si-O-Si bond. The bond observed near 994 cm−1 was assigned to the symmetric stretching of Al-O-Al in [AlO4]. The absorption bond observed near 1440 cm−1 corresponded to stretching vibration of B-O-B in [BO3]. In the network structure of the glass, Si4+ chiefly exists in the form of [SiO4], Si atoms were located in the center of the tetrahedron, and the O atoms were located in the four vertexes of the tetrahedron. The Si and O in the glass were mainly linked with the bridging oxygen of Si-O-Si. Al3+ chiefly exists in the form of [AlO4].
With the increasing of calcination temperature, some absorption bands that do not exist in the glass appear in the FT-IR spectra of glass ceramics. The band of bending vibration around 480 cm$^{-1}$ splits into two bands, and the same thing happened around 676 cm$^{-1}$, the intensity of absorption bands increases gradually and the frequency of the wave shifts to lower value, which indicates that the increase in the unsaturation degree of [Si-O] aggravates the fracture of network structure, and resulted in various kinds of network fracture. See table.1 for the wavenumber of main absorption peak of wollastonite glass ceramics with different sintering temperature.

| The calcination temperature (°C) | Maximum wavenumber of absorption peak (cm$^{-1}$) |
|----------------------------------|--------------------------------------------------|
| 20                               | 480 | 676 | 785 | 994 | 1444 |
| 800                              | 466 | 554 | 655 | 681 | 783 | 1019 |
| 850                              | 458 | 556 | 646 | 682 | 781 | 1023 |
| 900                              | 457 | 565 | 644 | 682 | 777 | 1018 |
| 950                              | 457 | 565 | 644 | 681 | 777 | 1020 |
| 1000                             | 456 | 565 | 644 | 683 | 777 | 1018 |

The FT-IR spectra of the glass ceramics with different content of gehlenite were displayed in Fig.2. Figure 2 shows the FT-IR spectra of glass ceramics prepared have five main absorption bands, the band near 470 cm$^{-1}$ could be assigned to the bending vibration of Si-O-Si linkages. The two bonds in the range of 640–690 cm$^{-1}$ were assigned to the vibration and stretching vibration of Si-O-Si in [SiO$_4$ ], respectively. The absorption peak at 777 cm$^{-1}$ belongs to bending symmetric stretching vibration of Si-O-Si bond or vibration of Al-O-Al in [AlO$_4$]. The bond observed near 1027 cm$^{-1}$ was assigned to the stretching vibration and bending vibration of Si-O-Si in [SiO$_4$].
Table 2 shows wavenumber of main absorption peak of wollastonite glass ceramics with different content of gehlenite, some absorption bands that do not exist in the glass appear in the FT-IR spectra of glass ceramics. The band of bending vibration around 470 cm$^{-1}$ splits into two bands, the intensity of absorption bands increases gradually and the frequency of the wave shifts to lower value, which indicates that the increase in the unsaturation degree of [Si-O] aggravates the fracture of network structure, and resulted in various kinds of network fracture. The peaks at about 777 cm$^{-1}$ were disappeared, and the weak peaks at 711 cm$^{-1}$ corresponding to wollastonite were found.

| The content of gehlenite (wt%) | Maximum wavenumber of absorption peak (cm$^{-1}$) |
|-------------------------------|-----------------------------------------------|
| 10                            | 469            -            646 684    -    777 1027 |
| 20                            | 470            -            565 649 684 -    776 1020 |
| 30                            | 460 475       565 646 684 -    777 1018 |
| 40                            | 460 477       565 650 684 711 -  1020 |
| 50                            | 448 481       565 643 684 711 -  1022 |

The FT-IR spectra of the glass ceramics with different holding time were displayed in Fig.3. Fig. 3 shows the FT-IR spectra of glass ceramics prepared with 0.5 h of holding time have six main absorption bands. The band located at 565 cm$^{-1}$ could be attributed to stretching vibration of [MgO4]. With the increasing of holding time, the band of bending vibration around 470 cm$^{-1}$ splits into two bands. This shows that when the holding time was more than 1h, it could result in various kinds of network structure fracture.
See Table 3 for the wavenumber of main absorption peak of wollastonite glass ceramics with different holding time. In conclusion, with the increase of sintering temperature, the absorption peak of 780 cm⁻¹ wave number weakens, indicating that the symmetric stretching vibration of Si-O bond and the stretching vibration of O-Al-O are weakened, indicating that the amount of gehlenite was reduced; with the increase of gehlenite content, the absorption peak of 777 cm⁻¹ wave number weakens, indicating that the symmetric stretching vibration of Si-O bond and the stretching vibration of O-Al-O are weakened. And after 0.5h of heat preservation, two absorption peaks of the wollastonite glass ceramics were added at 565 cm⁻¹ and 645 cm⁻¹, and a absorption peak appeared at 456 cm⁻¹ when the time was extended to 1h, which were caused by Ca-O stretching vibration absorption, indicating that wollastonite crystal was obtained. The position and intensity of the infrared absorption peak of the glass ceramic samples hardly changed with the prolongation of the holding time.

Fig.4 shows the XRD patterns of sample, which was prepared under the following conditions: sintering temperature 900 °C, content of gehlenite with 30 %, holding time 2 hours. The principal crystalline phase was wollastonite and has a small amount of residual unresponsive gehlenite.

The scanning electron microscopy (SEM) photograph of the glass ceramics prepared under the above conditions was shown in Fig. 5. It can be seen that, they were a large number of flake like in the glass matrix which width was about 1 µm. This was consistent with the XRD results. The flake like crystals were wollastonite.

Table 3 Wavenumber of main absorption peak of wollastonite glass ceramics with different holding time

| The holding time (h) | Maximum wavenumber of absorption peak (cm⁻¹) |
|----------------------|---------------------------------------------|
|                      |                                             |
| 0                    | - 480 - 676 - 785 994 1444                  |
| 0.5                  | - 473 565 645 681 778 1023 -                |
| 1                    | 455 476 565 645 684 780 1022 -              |
| 2                    | 456 478 565 647 682 777 1018 -              |
| 3                    | 462 478 565 647 686 777 1021 -              |
| 4                    | 458 472 565 643 679 777 1021 -              |
4. Summary:
In this paper, the influence of the preparation technology, such as the content of crystallization promoter, sintering temperature and holding time, on the reaction crystallization process of glass ceramics was studied by infrared spectroscopy. The changes of the peaks and the valence bond strength of wollastonite glass ceramics were analyzed.

The flake like wollastonite glass ceramics can be obtained by changing the sintering temperature, content of gehlenite and holding time use reaction crystallization method. The research of infrared spectrum shows that with the increasing of each preparation condition parameter, the increase of [Si-O] unsaturated degree will aggravate the fracture of network structure and lead to various network fractures. The optimum preparation conditions were as follows: sintering temperature 900 ºC, content of gehlenite with 30 %, holding time 2 hours. The results show that it is feasible to prepare wollastonite glass ceramics by reactive crystallization sintering method, and the change of reactive crystallization process can be analyzed by infrared spectrum, which is worth further application to other kinds of glass ceramics.

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