Preparation and Characterization of Transparent Glass Ceramics Containing Na₃Gd(PO₄)₂

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Abstract. Transparent glass ceramics with the mole percent composition of 21.3Na₂CO₃-2.2Gd₂O₃-38SiO₂-36.5H₃BO₃-2.0P₂O₅ were prepared by melting crystallization method. The heat treatment system, crystal phase, micromorphology and transmittance of the samples were tested and characterized by differential scanning calorimetry analysis(DSC), X-ray diffraction (XRD), scanning electron microscopy(SEM) and UV-Vis-NIR, respectively. The optimum heat treatment condition is 730°C for 2h. The Na₃Gd(PO₄)₂ crystal phase were precipitated homogeneously among the glass matrix. The results of FTIR spectra confirmed the presence of PO₄ groups in the glass ceramics samples. The refractive index of glass ceramics and glass samples were measured. In the visible region, the transmittance of glass ceramics is up to 80%.

1. Introduction
In recent years, the research on glass-ceramics has attracted wide attention. Glass-ceramics is a new type of composite material of crystalline phase and glass phase obtained by heat treatment of precursor glass material and proper control of crystallization time. Crystals in glass-ceramics are formed by nucleation and grain growth after heat treatment [1-8]. Therefore, glass-ceramics have the common advantages of both glass and crystal, which are easy to prepare, good transmittance and stable physical and chemical properties. It has been applied in thermology, chemistry and biology. Among them, phosphate glass-ceramics with moderate phonon energy, low scattering, high refractive index and energy transfer efficiency between phosphate glass-ceramics ions have become a research hotspot in recent years [9-15]. For example, Tomasz K. Pietrzak et al. studied the preparation of nano-sized Li₃Me₂(PO₄)₂F₃ glass-ceramics, using different transition metals (Me = V, Fe, Ti) doped LiF-Me₂O₃-P₂O₅ glass-ceramics, and their effects on the formation and crystallization of glass matrix[16]. S. Suresh, T et al. studied the effect of nickel ion coordination on the spectral properties of multi-component CaF₂-Bi₂O₃-P₂O₅-B₂O₃ glass-ceramics [17]. Swati Soman et al. studied the effect of isothermal heat treatment on the phase transition, microstructures and ionic conductivity of Li₂O-Al₂O₃-TiO₂-P₂O₅ glass-ceramics [18].

Transparent glass-ceramics containing Na₃Gd(PO₄)₂ crystal were prepared by melt crystallization method. The structure of precursor glass and glass-ceramics was studied, and the effect of heat treatment on the morphology of samples was analyzed. Infrared spectroscopy was used to study the microstructural changes of precursors glass and glass ceramics before and after heat treatment.
2. Experimental

Glass samples with a mass percentage ratio of 21.3Na₂CO₃-2.2Gd₂O₃-38SiO₂-36.5H₃BO₃-2.0P₂O₅ were prepared by melting method. The purity of Gd₂O₃ was 99.99%, and the other reagents were analytically pure. Batches of about 20g raw materials were well mixed in a mortar, covered corundum crucibles under air atmosphere, the mixed materials were heated at 1200°C for 1h in a resistance furnace with the heating rate of 2°C/min, and then the system was heated up to 1400°C for 2h. Subsequently, the melt was transferred into a steel mold, followed by annealing at 450 °C for 2 h, then the glass was cooled to room temperature with the annealing furnace, and the transparent glass sample which eliminates the internal stress labeled PG. After heat treatment the samples were transformed into glass ceramics. The samples of glass ceramics were cut into small pieces with the size of 10 mm × 10 mm × 2 mm and polished for other tests.

The differential scanning calorimetry (DSC) analysis of glass powder was carried out by using SDT 2960 thermal analyzer of TA Company in the temperature range of 200 ~900 C/min at a heating rate of 10 C/min. During the measurements A₁₂O₃ was used as a reference. Glass ceramics samples were ground into fine powder in agate mortar, and the 2500v X-ray diffraction analyzer of Rigaku company in Japan was used to determine the glass ceramics under different heat treatment conditions. The X-ray diffraction apparatus with Cu Ka radiation over the angular range 10 ~ 90° in a step size of 4°/min. The transmittance of the samples was measured by Ultraviolet-Visible-Near Infrared Spectrophotometer of Shimadzu (Shimadzu, UVMIN-1240) in the range of 0-1100 nm. The microstructure of glass ceramics was characterized by scanning electron microscopy (SEM, JEOL, JSM-7610F) operated at 10kV. The refractive index of samples was measured by Abbe refractometer (2WAJ). The Fourier transform infrared spectra of the samples were taken using a FTIR-8400S spectrometer in the wave number range of 1500-400 cm⁻¹. KBr pellets were used to record the FTIR spectra of the samples.

![Figure 1. The DSC curve of the Na₂O-Gd₂O₃-P₂O₅-SiO₂ system PG.](image)

| Sample number | Heat treatment temperature | Heat treatment time |
|---------------|----------------------------|--------------------|
| GC1           | 730°C                      | 1h                 |
| GC2           | 730°C                      | 2h                 |
| GC3           | 730°C                      | 3h                 |
3. Result and discussion

Figure 1(a) shows the DSC curve of the precursor glass. As seen in Figure 1, there is a distinct exothermic peak at 730°C. On the basis of DSC and experiment, the detailed heat treatment system of glass samples are established and shown in Table 1.

Figure 2 shows the X-ray diffraction patterns of glass PG and glass-ceramic samples GC1-GC3. After comparing the diffraction peaks with PDF standard cards, the crystal phase of the sample was determined to be monoclinic hexagonal Na₃Gd(PO₄)₂ (38-0059). The XRD pattern of sample PG shows no diffraction peaks characteristic, and the broad band is from typical amorphous SiO₂, indicating that it is completely amorphous. After heat treatment, some obvious diffraction peaks appeared in samples GC1, indicating that the sample has crystalline phase. With the increase of crystallization time, the diffraction peaks of sample GC2-GC3 increase and sharp peaks appear, which indicates that the crystal content is increasing gradually. According to the differential thermal analysis diagram of the sample, the phosphate glass-ceramics with high crystallinity and uniform grain size can be obtained. The optimum heat treatment condition is to keep the glass-ceramics at 730°C for 2 h. At the same time, the grain size is analyzed and calculated by Scherrer formula (1):

\[
D = \frac{k\lambda}{\beta \cos \theta}
\]

Where, D is grain size, K is constant 0.943, and \( \beta \) is half-peak width and height. It is converted into radian system, that is, \( \beta = (\text{FWHM}/180) \times 3.14 \). According to the calculation, the grain size of the sample is about 254 nm.

Figure 3 shows the SEM images of PG and glass ceramics under different heat treatment system. From the picture, it can be seen that there is almost no crystal phase in PG. The sample GC1 has grains with uneven size and low crystallization degree. With the increase of crystallization time, the growth of GC2 grains increases and the size is uniform, and the morphology is spherical. The grain size of...
sample GC3 increases, and the initial distribution of non-uniform particle size varies greatly, resulting in irregular shape and obvious agglomeration. The results show that the crystallinity increases with the increase of crystallization time, and the grain size and quantity also increase. The crystallization time is an important factor affecting the growth and distribution of grains.

Figure 3. SEM images of glass and glass ceramics under different heat treatment system.

Figure 4 shows the transmittance curves of glass sample PG and glass ceramics samples GC1-GC3. From Figure 4, it can be seen that the transmittance of GC1 is higher in infrared-visible region. The SEM images show that there are fewer grains in the sample GC1, which has less influence on the refractive index and reflection of light. The transmittance of sample GC2-GC3 decreases because of the increase of grains and crystallization degree in glass-ceramics, in which the transmittance of sample GC3 is the lowest, because with the increase of heat treatment time, the crystal grains grow and increase, and the phenomenon of agglomeration occurs, which reduces the gap between crystals, increases light scattering and diffraction, and increases light loss. It is noticeable that the transmittance of all samples tend to decrease at 435 nm. This effect is more prominent with increasing crystallization degree. This phenomenon could be explained by Henry theory, in which the intensity of scattered light in GC follows a $\lambda^6R^4$ relationship, where $\lambda$ is the wavelength of light and R is the average radius of crystals in GC [19]. So the transmittance of GC decreases with the decrease of wavelength as the grain size increases. The refractive index of samples are shown in Table 3. As shown in Table 2, the refractive index of PG is similar to that of GC1 and GC2, but the refractive index of GC3 is much larger than that of GC1 and GC2. This indicates that the grain size of glass-ceramics increases with the increase of heat treatment time, the grain size becomes larger, the refractive index increases and the transmittance decreases.

Figure 4. The optical transmittance spectra of PG, GC1, GC2 and GC3.
Table 2. The refractive index of samples.

| Sample number | Refractive index |
|---------------|-----------------|
| PG            | 1.5075          |
| GC1           | 1.5107          |
| GC2           | 1.5118          |
| GC3           | 1.5206          |

Figure 5 shows the infrared spectra of glass ceramics GC1-GC3 in the frequency region between 400 and 1400 cm\(^{-1}\). FTIR bands of the samples and their assigned vibrational modes are listed in Table 3. The band of GC1-GC3 at 465 cm\(^{-1}\) corresponds to the bending vibration of Si-O-Si bond in [SiO\(_4\)]; the bands between 565 cm\(^{-1}\) and 714 cm\(^{-1}\) correspond to the bending vibration of P-O-P bond in [PO\(_4\)]. With the increase of heat treatment time, the band decreases gradually, the vibration of P-O-P bond decreases, the number of crystals increases, and the absorption band widens, which indicates that the crystallization rate of glass-ceramics increases. The band at 818 cm\(^{-1}\) is due to the stretching vibration of Si-O bond in [SiO\(_4\)], and the band at 1028 cm\(^{-1}\) is attributed to the asymmetric stretching of Si-O bond in [SiO\(_4\)]. The band at 1204 cm\(^{-1}\) and 1394 cm\(^{-1}\) is due to the asymmetric stretching of B-O bond in [BO\(_3\)]. The formation of new crystalline phase was proved again by infrared spectroscopy. The results of XRD diffraction and SEM under different heat treatment conditions are consistent. It is shown that the grain size increases with the increase of heat treatment time at constant temperature.

Table 3. Assignment of FTIR bands of the samples.

| Peak position | Assignments                                      |
|---------------|--------------------------------------------------|
| 465           | bending vibration of the Si-O-Si                 |
| 562           | P–O–P bending vibration                          |
| 714           | vibration modes of symmetric stretching of P-O-P |
| 818           | stretching vibration of Si-O-Si of SiO\(_4\) tetrahedron |
| 1028          | asymmetric stretching of Si-O bonds              |
| 1204          | B-O asymmetric stretching modes of BO\(_3\)     |
| 1394          | asymmetric stretching modes of BO\(_3\) triangular |
4. Conclusions
Glass ceramics with Na$_3$Gd(PO$_4$)$_2$ crystalline phase were prepared by melt crystallization method for the first time. The optimum heat treatment condition was determined to be 730°C crystallization for 2 h. The transmittance of glass-ceramics in visible region is 80%. The crystal grain size is 254 nm. It is proved that with the increase of heat treatment time, the transmittance of glass-ceramics decreases and the refractive index increases.

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