Preparation and optical properties of boron-doped Si-Na-Al-Zn photo-thermal-refractive glass

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Abstract. Photo-thermo-refractive (PTR) glass, which has the advantages of high refractive index modulation value, large working bandwidth and wide environmental adaptability, is an excellent material for preparing volume Bragg grating (VBG). However, the application of PTR glass is limited because of its high melt processing temperature and high optical loss. The introduction of boron into PTR glass can significantly reduce the melting temperature. In this study, boron-doped Si-Al-Na-Zn PTR glass was prepared at a low temperature by the high-temperature melting method, and its temperature–viscosity relationship, heat treatment procedure and optical properties were investigated. The results show that the introduction of boron into PTR glass can significantly reduce the high-temperature viscosity of PTR glass. The melting temperature is lower than 1,400 °C, and the optimum nucleation and crystallisation temperatures are 490 °C and 590 °C, respectively. The optical transmittance of UV-exposed and heat-treated glass is more than 90%, which indicates its excellent optical properties and its applicability for use in preparing VBG with high diffraction efficiency and low optical loss.

1. Introduction
In recent years, with the development of laser technology, particularly high-energy laser technology, volume Bragg grating (VBG) has important applications in improving laser beam quality, such as reducing the laser system volume and stabilising the laser output spectrum [1]. Holographic recording materials, silver halide gel, lithium niobate crystal and dichromate, which can be used to prepare VBG, have disadvantages, such as low refractive index modulation value, poor stability and poor environmental adaptability, which limit its application [2]. Photo-thermo-refractive (PTR) glass is an optical material that can induce the precipitation of NaF crystallites after UV exposure and heat treatment. The refractive index difference between crystallite and glass matrix can be utilised as reference holographic information during the preparation of VBG. As a new type of photosensitive material, PTR glass can compensate for the disadvantages of traditional holographic recording materials and has the advantages of high laser damage threshold and wide working range, which make it the best holographic material for VBG [3].

Researchers at the University of Central Florida in the United States began research on PTR glass in the Si-Al-Na-Zn system in 1990[3]. The PTR glass of this system has high viscosity at high temperature and requires a high melting temperature (higher than 1,500 °C) and a long melting time, which leads to
the high volatility of glass components, such as NaF, at high temperature, influencing the stability of glass components. Researchers at Jena University in Germany used CaF$_2$, which has higher solubility in the glass matrix, to replace NaF. This type of PTR glass can precipitate more CaF$_2$ crystallites after UV exposure and heat treatment, and its refractive index modulation value is theoretically slightly improved. However, it is difficult to reduce the melting temperature of PTR glass in the system because of its high-temperature viscosity [4]. In 2013, the Xi’an Institute of Optics and Fine Mechanics of the Chinese Academy of Sciences conducted a study of boron-doped PTR glass. The results show that the introduction of boron can effectively reduce the high-temperature viscosity of PTR glass [5]. However, studies of the nucleation and crystallisation heat treatment processes and optical properties of boron-doped PTR glass are rare.

According to previous research, the UV exposure and heat treatment processes are as follows: The first step is the photo-ionisation of Ce$^{3+}$:

$$\text{Ce}^{3+} + h\nu \rightarrow \text{Ce}^{4+} + e^-$$

Then, the electron will be trapped by the silver ion:

$$e^- + \text{Ag}^+ \rightarrow \text{Ag}^0.$$  

Subsequently, the glass will undergo nucleation heat treatment, in which Ag$^0$ will aggregate into silver clusters:

$$n\text{Ag}^0 + T_1 \rightarrow \text{Ag}_n^0.$$  

The crystallisation heat treatment will follow. In this process, heterogeneous precipitation of NaF microcrystal on top of Ag$^0$ will form. Compared with the glass matrix, its refractive index will have a decrement of approximately 1,000 ppm.

These features ensure that PTR glass is a suitable holographic recording material for the preparation of VBG. However, it is difficult to manufacture PTR glass because of the high melting temperature of PTR glass in the Si-Al-Na-Zn system. This study proposes a new system with PTR glass that has a low melting temperature, which makes it easier to manufacture. The heat treatment procedure and optical properties will also be investigated.

2. Experiment:

In this study, glass composed of $(70 - x)\text{SiO}_2 - x\text{B}_2\text{O}_3 - 16\text{Na}_2\text{O} - 8(\text{ZnO} + \text{Al}_2\text{O}_3) - 5\text{NaF} - 1\text{KBr}$ (mol%), where $x$ is equal to 0 and 5 mol%, was developed using a two-step melting method. Parent glasses were denoted as AgNO$_3$, CeO$_2$, SnO$_2$ and Sb$_2$O$_3$. The glass was subjected to the melting, stirring and clarification processes. The melting temperature was 1,350 $^\circ$C to 1,400 $^\circ$C, and the melting time was 6–8 h. After the glass was melted, it was annealed at 460 $^\circ$C. The annealed glass was cut into 10 mm × 10 mm × 3 mm sheet samples and polished for UV exposure and heat treatment experiments. Exposure was conducted using a 50 mW 325 nm He–Cd laser (Kimmon IK3501) with an exposure dose of 4 J/cm$^2$. The sample was uniformly exposed, that is, the beam was collimated, expanded and directly irradiated onto the sample surface.

3. Results and Discussions

3.1. Effect of boron on high-temperature viscosity

Conventional PTR glass is a silicate glass with a silicon content of approximately 70%. The high-temperature viscosity of liquid glass makes it difficult to clarify, stir and pour at a high temperature. Thus, it is necessary to lower the high-temperature viscosity of glass. One method is to introduce boron into the silicate glass system. After boron is doped, boron forms a part of oxygen in [SiO$_4$] in the glass [BO$_3$] and [BO$_4$], where [BO$_3$] is layered [6]. The bond strength is weakened, and the viscosity of glass is reduced. On this basis, two PTR glasses were designed and prepared in this study. The matrix components are shown in Table 1.
Table 1. Composition of B0 and B5 glass

|     | Composition                                                                 |
|-----|-----------------------------------------------------------------------------|
| B0  | 70SiO$_2$ − 16Na$_2$O − 8(ZnO + Al$_2$O$_3$) − 5NaF − 1KBr                   |
| B5  | 65SiO$_2$ − 5B$_2$O$_3$ − 16Na$_2$O − 8(ZnO − Al$_2$O$_3$) − 5NaF − 1KBr     |

In this study, a rotary viscometer is used to measure the high-temperature viscosity of B0 and B5 glass. Then, the AM equation is selected on the basis of the disorder of atomic motion introduced by Avramo et al. The AM equation uses atomic jump to describe the supercooled liquid. According to the stochastic distribution theory of molecular or atomic kinetic energy, molecular motion is caused by structural disorder [7]. The AM equation is expressed as follows:

$$\log(T, x) = \log_{\infty} \eta(x) + \left(\frac{T}{T_g}\right)^{\alpha}$$

Where $\tau$ and $\alpha$ are the fitting parameters and $\log(T, x)$ is the viscosity of glass at the limit temperature.

Figure 1 shows the viscosity measurement values and fitting results of B0 and B5 glass obtained using Formula (1).

3.2. Effect of heat treatment duration and temperature on the nucleation and crystallisation processes

PTR glass must undergo UV exposure before heat treatment, and Ce$^{3+}$ in the glass is ionised to release electrons during UV exposure. Immediately after heat treatment, the first stage is the nucleation process (heat treatment temperature is $T_1$) and the second stage is the crystallisation process (heat treatment temperature is $T_2$). On the basis of the temperature characteristics, the heat treatment process of PTR glass is characterised as follows:

1. When $T_g < T \leq T_1$, the formation process of crystal nuclei increases with the increase in the number of crystal nuclei.
2. When $T_1 < T \leq T_2$, NaF crystallites appear; when $T = T_2$, the rate of NaF crystallites is the largest.
3. $T_2 < T \leq T_m$, where $T_m$ is the melting temperature of NaF crystallites in the vitreous material, and the NaF crystallites formed at this time start to dissolve.

The heat treatment procedure is shown in Table 2. Figure 2 shows the absorption peak of PTR glass in two heat treatment stages at 400–500 nm.
Table 2. Temperature and time of the nucleation and crystallisation heat treatment processes

| No. | $T_1/\degree C$ | $t_1/h$ | $T_2/\degree C$ | $t_2/h$ |
|-----|----------------|---------|----------------|---------|
| 1   | 470            | 8       | 550            | 8       |
| 2   | 470            | 4       | 570            | 4       |
| 3   | 470            | 2       | 590            | 2       |
| 4   | 490            | 8       | 570            | 2       |
| 5   | 490            | 4       | 590            | 8       |
| 6   | 490            | 2       | 550            | 4       |
| 7   | 510            | 8       | 590            | 4       |
| 8   | 510            | 4       | 550            | 8       |
| 9   | 510            | 2       | 570            | 2       |

Figure 2. Absorption peak value of B5 glass that underwent nucleation and crystallisation heat treatment processes

After nucleation heat treatment, PTR glass needs to have as many crystal nuclei as possible to promote the formation of crystallites, that is, it requires high absorption at the characteristic absorption peak (400–600 nm) of the crystal nucleus. Meanwhile, low absorption after crystallisation heat treatment is required to reduce optical losses. In summary, the optimal post-processing procedure, that is, 490 °C/4 h and 590 °C/8 h, is utilised to obtain the experimental results for sample #5. Figure 3 shows the change in transmittance of the glass at various stages of heat treatment at 490 °C/4 h and 590 °C/8 h.

Figure 3. Transmittance spectra of different stages

(Inset: (a) original glass; (b) glass with UV exposure and nucleation heat treatment processes; (c) glass with UV exposure nucleation and crystallisation heat treatment processes)

Figure 3 shows that the PTR glass that has not undergone any treatment has a transmittance of more than 90% in the 400–2,600 nm band. The absorption of PTR glass in the 400–600 nm range is significantly enhanced after nucleation heat treatment, which indicates that a large number of silver particles is formed in PTR glass as crystal nucleus after nucleation heat treatment. The absorption is
significantly weaker after crystallisation heat treatment. The transmittance of PTR glass after crystallisation heat treatment is more than 90% in the 400–2,600 nm band, which has excellent optical properties and is beneficial for the preparation of low-optical-loss devices, particularly for VBG.

4. Conclusion
In this study, boron-doped PTR glass was prepared at a low temperature by the high-temperature melting method. The high-temperature viscosity of boron-doped PTR glass was experimentally measured and theoretically analysed. The results show that the introduction of boron into PTR glass decreased the high-temperature viscosity of PTR glass and induced the melting of PTR glass at low temperature. The stability of the components of PTR glass is improved. The best heat treatment procedure for boron-doped PTR glass is nucleation. The results show that UV-exposed and heat-treated glass has an optical transmittance of more than 90% and has low optical loss, which lays the foundation for the preparation of VBG with low optical loss.

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