Thermally induced nanocrystallization in SrO-TiO_2-SiO_2 glasses tracking by the Maker fringe patterns analysis

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Fresnoite-type nanocrystallized $2.0SrO$-$1.0TiO_2$-$2.9SiO_2$ glass was prepared by the conventional melt-quenching method. With Maker fringe patterns of several annealing conditions, the time-dependence and temperature-dependence of crystallization dynamics was discussed. The UV-Vis-IR measurements showed that its transmittance decreased with the increasing of annealed temperature, which indicated the appearance of crystallite phase in glass. Different trends of Maker fringe patterns corresponding with different crystallization process were discussed, which was also confirmed by XRD and SEM measurements. Maker fringes measurements can be performed not only as a second-harmonic generation characterization method but also as a means to study the crystallization process in glass.

(Received March 11, 2012; accepted October 30, 2012)

Keywords: SrO-TiO2-SiO2 glasses, Nanocrystallization, Maker fringe, Second harmonic generation, Dynamics

1. Introduction

In the past few years, the nonlinear optical materials have attracted much attention due to their application in optical telecommunications [1-2]. Nonlinear optical glass-related materials have been widely studied according to their advantages, such as large Kerr nonlinearity, high second-order nonlinear effect, low cost, and easy processing so on [3-4]. Recently, transparent crystalline glasses consisting of optical non-linear crystals have been investigated for their large second susceptibility [5-6] to apply to laser hosts, tunable waveguides, tunable fiber gratings and other optical applications [7-9].

Transparent crystalline glasses with different crystals have been studied for their excellent properties, for example langasite-type $La_3Ga_5SiO_{14}$ crystals with great piezoelectric properties [10], stillwellite-type $LaBGeO_5$ crystals with ferroelectric properties [11] and benitotie-type $Ba_2TiGe_3O_9$ crystals with their attractive nonlinear optical properties [12]. Especially the fresnoite-type crystals in transparent crystalline glasses attracted much attention due to their large second-order optical nonlinearity, such as in $Ba_2TiSi_2O_8$, $Ba_2TiGe_2O_8$ and $Sr_2TiSi_2O_8$ crystallized glasses [13-18]. Although these crystals show large second-order nonlinearity, their birefringence in the visible spectra is too small to allow phase matched Second Harmonic Generation (SHG) [19]. So materials with fresnoite-type structure by substituting Sr^{2+} for Ba^{2+} has been widely investigated with their crystallization [20] and optical properties [21]. We also reported that $Sr_2TiSi_2O_8$ crystallite phase was prepared by isothermal oriented crystallization with additional applied electric [22]. In these papers, the crystallization mechanism was usually studied with crystal growth kinetics and activation enthalpies for viscous flow, structural units transporting across the nucleus/melt interface (nucleation) and crystal growth [23]. However, to our knowledge, there are few reports to investigate the dynamics of crystallization in $Sr_2TiSi_2O_8$ glasses with Maker Fringe patterns. In this paper, we synthesized $Sr_2TiSi_2O_8$ glasses with fresnoite-type crystalline structure by the melt-quenching method, and discussed the influence of thermal conditions on second harmonic (SH) intensity to investigate the dynamics of thermal induced crystallization by the means of Maker fringe patterns.

2. Experimental

Fresnoite-type crystallized $2.0SrO$-$1.0TiO_2$-$2.9SiO_2$ (mol %) bulk glass was prepared using the conventional melt-quenching method. In a typical experiment, $SrCO_3$ (99.95%), TiO_2 (99.9%) and SiO_2 (99.9%) were mixed and well melted in a platinum crucible at 1450°C for 2 hours and then quenched on a steel plate at 200°C. The annealing was performed at 650°C for 12h. Glass plates of dimensions of $\Phi 20 \times 1 mm^2$ were cut from bulk glass and mechanically polished to optical quality on both sides. Crystallization was carried out by heating samples

with different temperatures ($T_{HT=}$790°C, 810°C, 830°C, 850°C, 870°C, 890°C, 910°C) with the heating rate of 5°C /min and different period (2h, 3h, 4h and 5h).

The optical absorption spectra were recorded with a UV-Vis-near IR Spectrophotometer (Shimadzu UV-1601) in the region of 200-1100 nm with the resolution of 0.5nm.The SH intensities of samples were measured using a pulsed Nd: yttrium-aluminum-garnet (YAG) laser with a pulse width of 10 ns[7]. The fundamental wave at 1064 nm was used as the incident light. The output light from the glass plate passed through a filter to split the SH wave at 532 nm from the fundamental wave. The measurements were performed at consecutive angles of incidence from -80° to 80° with the samples placed on a rotating stage. A α-quartz (Z-cut, thickness=0.782 mm) was used as reference to adjust the Maker fringe measurements. The crystalline phase was examined by X-Ray Diffraction (XRD, XRD-Rigaku Ultima III) at room temperature using Cu Kα radiation and the thickness of crystallization layer in the surface layer was characterized by Scanning Electron Microscope (SEM, JSM-5610LV) .

3. Results and discussion

Wang et al [22] reported that $Sr_2TiSi_2O_8$ crystal performed oriented growth with polarizability along c-axis. This kind of fresnoite-type structure is flat sheets made up of $[Si2O_7]^{6-}$ which are linked to TiO_5 pyramidal units. These stacks of sheets are held by large ions presented in coordination polyhedra [24]. The research of crystallization process in these transparent crystallized glasses usually needs more microscopy photos or spectra to provide the evidence of changes occurred in materials. Tanakashi et al [12] also reported that the temperature of the crystallization was a key factor in the second-order nonlinearity of $Sr_2TiSi_2O_8$, but the proper ranges of temperature and time in the heat-treatment have not given yet for a good performance on nonlinear optical properties. At the same time, it will be better to perform a direct method to investigate the thermal crystallization process of these materials. So in this paper, we tried to make full use of Maker fringe patterns of transparent $2.0SrO\text{-}1.0TiO_2\text{-}2.9SiO_2$ glasses to study their crystallization dynamics at different annealing conditions.

The UV-vis-near IR transmission spectra of $2.0SrO\text{-}1.0TiO_2\text{-}2.9SiO_2$ glass samples are shown in Fig. 1. The transparent crystallized glasses were annealed for 2 hours at 790°C, 810°C, 830°C, 850°C, 870°C, 890°C and 910°C, respectively. All samples have a wide transmission window from NIR to UV with an absorption edge around 340nm which meant that these samples have almost the same optical band gap as as-treated glasses. The transmittance of these samples decreases quickly with increasing heat-treatment temperature from 830°C to 870°C comparing to the ranges from 0°C to 830°C and from 870°C to 910°C . These transmission spectra give the evidence of the information of crystallization in glass with heat-treatment.

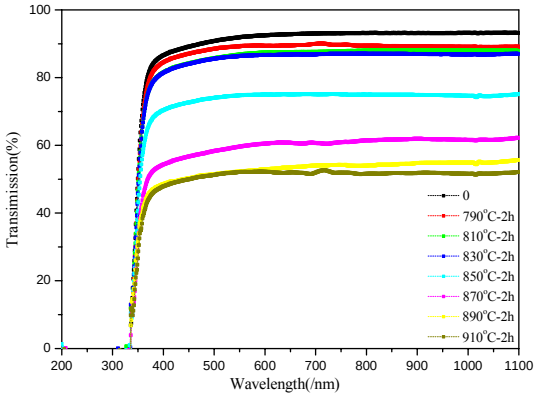

Fig.1 UV-Vis-near IR optical transmission spectra for as-treated samples and heat-treated glasses at $T_{HT=}$ 790°C -910°C for 2 h.

The Maker fringe patterns of transparent crystallized glasses with annealing from 790°C to 910°C for 2 hours are shown in Fig. 2. Obvious SH signals were observed at T_{HT} =850-910 °C for 2 hours , while no SH signal was detected at T_{HT} =790-830°C. And the intensity of SH increased with the increasing of temperature. However, the patterns of Maker fringe tend to become broader and the maximum intensity shifted from θ=±40° to θ=0° when temperature was higher than 890°C. It was reported that TiO_5 pyramidal unit included one short Ti-O bonds along the c-axis and four longer Ti-O bans along the a-axis [24], which was the origin of large SHG in fresnoite-type crystals such as $Ba_2TiGe_2O_8$ crystal. So we speculated that enough non-central symmetry crystals in the surface layer or bulk would interrupt the symmetry and induce SHG in glasses.

To clarify our speculation, the surface XRD analyses were done in the as-treated and treated samples at 850°C. We chose three samples with characteristic Maker fringe patterns to investigate: as-treated glass, and heat-treated samples at 850°C and 910°C, both for 2 hours. It is clearly shown in Fig. 3 that there is no obvious crystallite phase for the as-treated glass. And at 850 °C, the relative intensity of peaks related to $Sr_2TiSi_2O_8$ phase increased strongly. When the temperature was up to 910 °C, the intensity of this strong peak increased slightly but the other tiny peaks corresponding to different plans became obvious.

In order to observe the thickness of crystallization layer in glasses, figure 4 shows the SEM image of the surface and the cross-section (insert picture) of the heat-treated sample at 850°C for 2h. White points in the image represent crystallites, which are distributed almost homogeneously in the sample surface layer. The thickness of the layer is 15 μm. From the cross-section

photograph, it indicated that the nucleus of crystallite grew and crystallized firstly in the surface and later in the interior of samples.

In the view of the SH signal appearance at 850 °C for 2h, the temperature 850°C was selected as a significant temperature to investigate crystallization process by Maker fringe patterns. Figure 5 gives the result of Maker fringe measurements of samples annealed at 850°C for 2, 3, 4 and 5 hours. The SH intensity increased drastically with heat-treatment time from 2 to 3 hours. However, when the heat-treated time increased, the relative SH intensities of samples with heat-treatment time from 3 to 5 hours did not increase drastically. But, the pattern of fringes became broader and the maximum value also shifted from around θ=±40° to θ=0°, which was similar to the crystallization of samples annealed at different temperatures in Fig. 2.

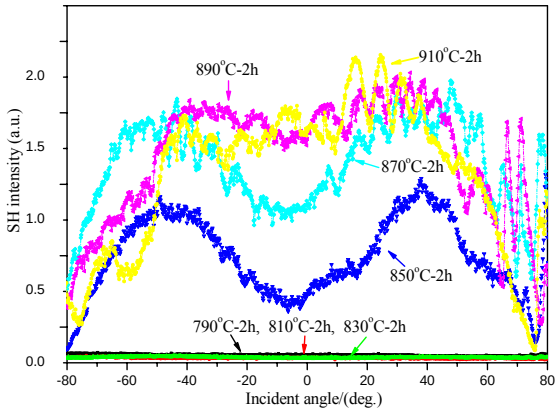

Fig.2 Maker fringe patterns for transparent crystallized glasses obtained by heat-treatments at $T_{HT=}$ 790°C -910°C for 2 h.

In our experiments, when the samples were heat-treated in a critical condition, the nucleus grew and crystalline phase began to appear in glasses. It is observed from Fig. 2 that there is no SH signal detected when the temperature increased from 0 to 830°C, which means that there is no or little non-central symmetric crystalline phase in glasses. When the temperature was up to 850°C, SH signals could be detected as shown in Fig. 2. At this time, the nucleuses were formed easily in the surface layer because its nucleation energy was lower than that in the interior of glasses, and then grew freely in different direction. Small crystallites appeared and the surface crystallization was predominant.

The XRD patterns for 850°C-2h in Fig.3 showed that the crystallization of $Sr_2TiSi_2O_8$ crystallite phase corresponding to plan (002) appeared well in the surface layer. As the effect of dipole moments, these crystallites preferred to grow along the direction of c-axis which was perpendicular to the sample surface. When $Sr_2TiSi_2O_8$ crystallites own tetragonal structures with a space group P4bm at room temperature and TiO_5 units in which bond length along c-axis is much shorter than that in other directions, its lattice energy along c-axis is also larger than that in other directions which leads this kind of crystal to perform second-order nonlinear property [18], that is also why the transmission decreases drastically in Fig. 1. While the T_{HT} increased continuously, larger SH intensities in transparent glass was observed in Fig. 2 and 5, which meant crystallization occurring in the interior of samples. Meanwhile, when the samples were treated at higher temperature or with longer time, different densities between crystalline phase and glassy phase as shown in Fig. 4 affected the dimension (e.g. ratio c/a) of the TiO_5 unit cell. As the second-order nonlinearity increased with increasing ratio c/a [14], the performed larger SH intensities in Fig. 2 and 5 indicated that the occurrence of in unit cell dimension variation in glasses. But with increasing the temperature or time continuously, for example, when the treated temperature was higher than 890°C or the time was longer than 3 hours, there were no large differences of SH intensity among these samples. It is speculated that the nucleuses are formed more stably and epitaxy are fuller in glasses. Meanwhile, the amount of surface nucleation becomes lager and then tends to be saturated. Small granular crystals begin to appear in the interior of glasses. These granular crystals induce the disordered growth in glasses, but also prevent the grain orientating near to the surface. These were confirmed in Fig 3 that the intensity of tiny peaks corresponding different plans of the sample treated at 910°C for 2h became larger and the intensity of this strong peak increased slightly comparing to the sample treated at 850°C for 2h. At the same time, the scattering of SH waves by crystallites precipitate in the interior of glasses was contributed to broader Maker fringes patterns, and when the existence of grain boundary of crystals, the scattering of the incident and SH waves became minimum which induced the maximum SH intensity at the angle of 0°[25]. Therefore, the crystallization started from the surface to the interior of our glassy sample which was analyzed from Maker fringe patterns.

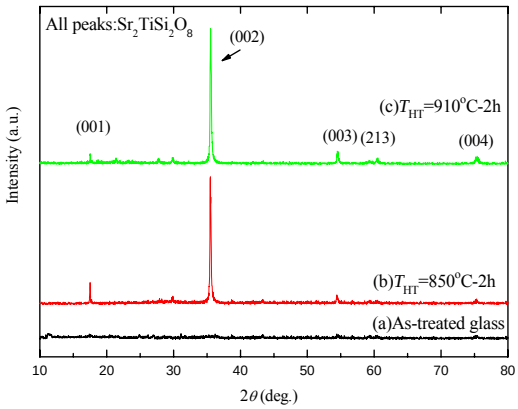

Fig.3 XRD patterns for the (a) as-treated glass and the surface region of transparent crystallized glasses heat-treated at (b) 850°C for 2h and (c) 910°C for 2h.

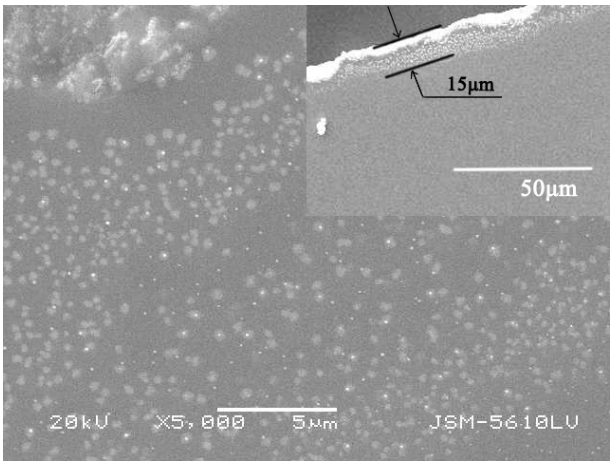

Fig.4 SEM images of the surface and the cross-section (insert picture) heat-treated at $T_{HT=}$ 850°C for 2h.

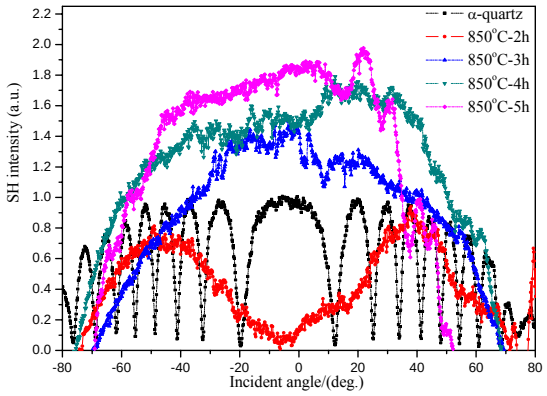

Fig.5 Maker fringe patterns of α-quartz and transparent crystallized glasses obtained by heat-treatments at $T_{HT=}$ 850°C for 2h-5h.

4. Conclusions

Fresnoite-type crystallized 2.0SrO-1.0TiO_2-2.9SiO_2 glass was prepared by conventional melt-quenching method. The Maker fringe patterns of different heat-treatment conditions were used to discuss the time-dependence and temperature-dependence of crystallization dynamics. The appearance of crystallite phase in glass induced the decline of transmittance with the augmentation of treated temperature. The different trends of Maker fringe patterns corresponded with different crystallization process, which was verified by XRD analyses and SEM images. It was indicated that the surface crystallized firstly and then the crystalline phase appeared in the interior of glasses. So Maker fringes measurement can be used as not only a characterization method for SHG but also a means to study the crystallization process in crystallized transparent glasses.

Acknowledgement

This research work was financially supported by the National Natural Science Foundation of China (51272183) , the Specialized Research Fund for the Doctoral Program of Higher Education (20090143110011) and the Program for Discipline Leader in Wuhan (201051730563).

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