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SiO_2-TiO_2 graded bulk glass prepared by sol-gel method and centrifugal processing

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Abstract

We had prepared SiO_2-TiO_2 graded glass by means of sol-gel method combined with centrifugal processing in previous study. However, the graded glass had many cracks. In this study, we intended to fabricate SiO_2-TiO_2 graded bulk glass without cracks by improvement of graded grass preparing process. The appearance of cracks was inhibited compared with the previous study. The results of the XRD and FT-IR revealed that the graded structure was continuous in molecular scale. The result of FT-IR showed that infra-red absorption peaks of Si-O-Si stretching and bending shifted with increasing the concentration of Ti.

1. Introduction

Several methods have been proposed to prepare functionally graded glasses. In the preparation of a planar microlens, circle-shape graded structures have been formed in small bulk glass samples by plasma CVD [1], a photochemical process [2], electromigration [3, 4]. Recently, sedimentation of the atoms was realized in alloys or compounds under an ultra-strong acceleration field of 1 million g level [5, 6]. However, it is expected that sedimentation of colloid particles can easily occur in liquid (sol) under a comparatively low gravity field due to the large molecular weights. We had prepared SiO_2-TiO_2 graded glass by means of sol-gel method combined with centrifugal processing [7]. However, the graded glass had many cracks. We assumed that it is due to weak strength of polymer. In this study, we intended to inhibit appearance of the crack by decreasing volume of ethanol for increasing density of the graded glass compared with previous study. Homopolymerization time was extended from 13 hours to 18 hours to prepare graded glass lower gravitational field. The characterization was investigated by means of an electron probe micro analyzer (EPMA) and a micro-area X-ray diffraction (XRD). In addition, we measured infra-red absorption spectrum to evaluate the optical properties by Fourier transform infrared (FT-IR) spectroscopy.

2. Experimental

The preparation procedure for the SiO_2-TiO_2 system which is same as that of the preparation process [8] is shown schematically in Fig. 1. The time of t_A was increased to 18 hours, and the total volume of ethanol was decreased to 2.55 ml (0.04376 mol) compared with the previous study. The time of t_B and t_C was 0.25 and 0 respectively, as well as previous one. The obtained bulk specimen was analyzed by EPMA, XRD and FT-IR.

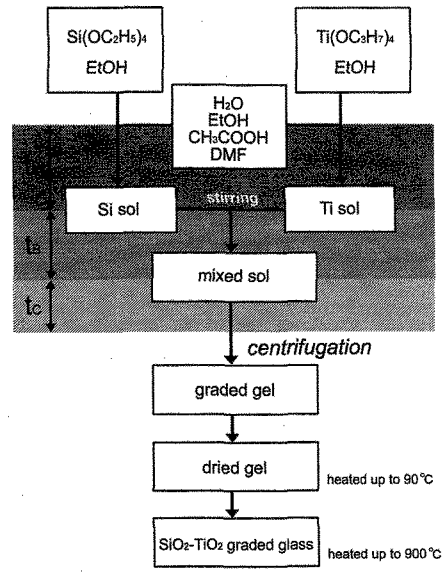

Fig. 1 Preparation process of SiO_2-TiO_2 graded glass

The procedure was: 3.88g (0.0186mol) of tetraethoxysilane ($Si(OC_2H_5)_4$) and 1.09 ml of ethanol (C_2H_5OH) were stirred in a vial at room temperature. Catalyst solution [0.71 ml (0.0039 mol) of water (H_2O), 1.09 ml (0.0372 mol) of ethanol, 4.5 ml (0.078 mol) of acetic acid (CH_3COOH) and the 1.36 g (0.0186 mol) of N,N-dimethylformamide (DMF: $(CH_3)NCHO$)] were added to the Si alkoxide solution under stirring for hydrolysis and polymerization. In another vial, 0.93 g (0.00328 mol) of tetraisopropoxytitan ($Ti(OC_3H_7)_4$) and 0.19 ml ethanol were stirred, as well as Si alkoxide solution. The catalyst solution [0.19 ml (0.011 mol) of water (H_2O), 0.19 ml (0.0372 mol) of ethanol, 1.2 ml (0.021 mol) of acetic acid (CH_3COOH) and the 1.36 g (0.0186 mol) of DMF] were added to the Ti alkoxides

solution under stirring. Both the solutions were kept 35~40℃ for homopolymerization for t_A (homopolymerization time) separately. After keeping for t_A at 35~40℃, Ti solution was added to the Si solution, and stirred for t_B (mixing time). The molar ratios of Si and Ti were 85 : 15 (mol%) in this study. The mixed sol was kept at t_C (copolymerization time). The mixed sol was put into a plastic tube with a diameter of 25mm and was centrifuged under a gravitational field of 7.5×10^3 G for 48 hours at about 40℃ using a centrifugation machine (H-2000RF of Kokusan, Ltd). White gel with a size of 10mm scale was obtained at the bottom of plastic tube. Finally, the gel was dried at 90℃ to remove the solvent, and heated up to 900℃ to obtain the SiO_2-TiO_2 glass.

3. Results and Discussion

The EPMA result of the specimen that had some crack is shown in Fig. 2. This is the photo mapping with the linear composition profiles of Si and Ti at the polished surface in which plane contained the rotation axis of the SiO_2-TiO_2 specimen. The number of crack was decreased compared with previous sample. The concentration of Si continuously decreased, while that of Ti increased in the direction of the gravitational field.

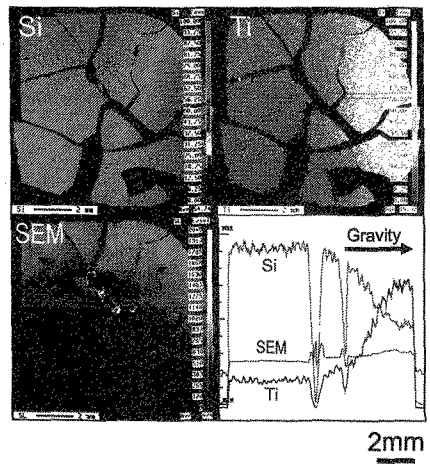

Fig. 2 EPMA result of SiO_2-TiO_2 sample (Si : Ti = 85 : 15 (mol%), t_A-t_B-t_C = 18-0.25-0, Maximum acceleration : 7,500

The XRD result that was measured the specimen at three points is shown in Fig. 3. The XRD pattern A and C were measured at higher and lower gravitational field point in the sample, respectively. The pattern B was measured the intermediate point. All patterns consisted of broad peak in the low diffraction angle range, which only differed slightly in shape. This showed that the specimen had a glass structure, and the graded structure was continuously in molecular scale.

The FT-IR result is shown in Fig. 4. Absorption bands around 800cm^{-1} and 1040cm^{-1} assigned Si-O-Si bending and Si-O-Si stretching, respectively [9]. Absorption band around 950cm^{-1} could be attributed to the Ti-O-Si bond [10, 11]. This result also means that the SiO_2 and TiO_2 were mixed in molecular scale. Absorption peak of Si-O-Si stretching was shifted from about 1040 cm^{-1} to about 1050cm^{-1}, while Absorption peak of Si-O-Si bending was shifted from about 790 cm^{-1} to about 780cm^{-1} with the concentration of Ti. The shift of that peaks is consistent to relation between the α-quartz and amorphous silica [12].We assumed that the distance between the Si atoms was increased, and the angle of Si-O-Si bonds also increased with the concentration of Ti [13].

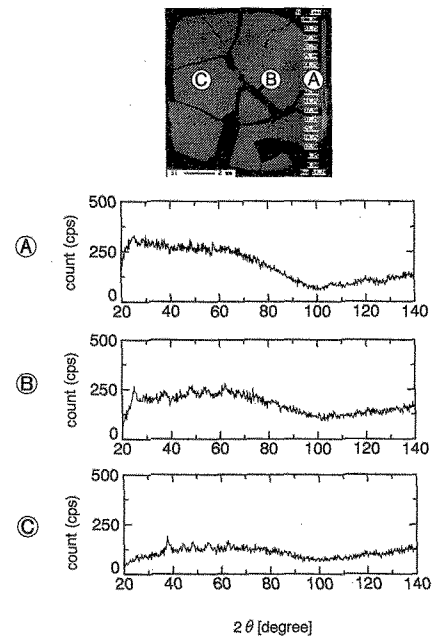

Fig. 3 XRD result of SiO_2-TiO_2 sample

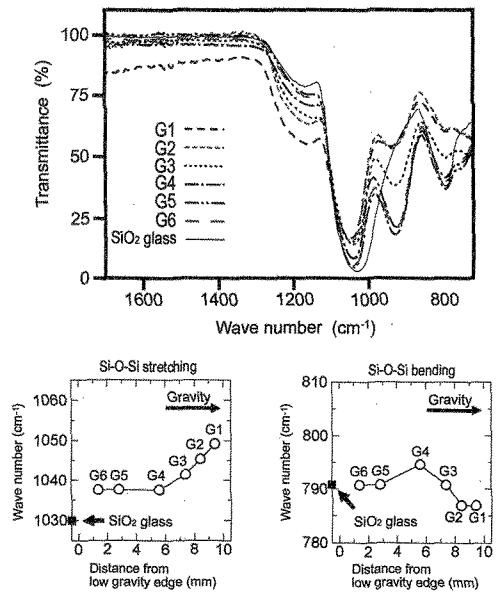

Fig. 4 FT-IR result of SiO_2-TiO_2 graded glass

4. Conclusion

The appearance of crack in SiO_2-TiO_2 graded glass was inhibited by means of decreasing volume of ethanol compared with the sample of previous study. The characterization was examined by EPMA, XRD and FT-IR. The result of FT-IR spectroscopy showed that infra-red absorption peak of Si-O-Si bending and stretching was shifted with increasing concentration of Ti. Graded glass is expected lens effect in the planar glass, prism effect, etc. The preparation of the graded glass of SiO_2-ZrO_2, SiO_2-VO_2, etc. is now under study.

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