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Articles

Graded Oxide Glasses in Binary Systems (Si−Ti, Si−V, and Si−Zr) Prepared by the Sol−Gel and Centrifugal Process

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The graded oxide glasses in binary oxide systems (Si−Ti, Si−V, and Si−Zr) had been prepared by means of a sol−gel method combined with centrifugal processing. In the Si−Ti and Si−V oxide systems, the graded oxide glasses, whose composition continuously changed with dimension in molecular scale, were prepared. The FT-IR analysis showed that infrared absorption peaks of Si−O−Si stretching and bending shifted, and Ti−O−Si or V−O−Si bands appeared with increasing the concentration of Ti or V, respectively. In the Si−Zr oxide system, the graded oxide glass in which the ZrO_2 nanocrystals appeared in the high gravity region was prepared.

Introduction

Transition metal oxide glasses have been used as colored window, light emitting, light catalyst materials and so forth. The graded oxide glasses or nanocrystal−glass composites are expected to show wide-range frequency light properties, to be used for IT or in the environmental industry, and so forth. 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] photochemical process,[2] electromigration,[3,4] ion exchanging, thermal diffusion of different compositions glasses, and so forth. Recently, one of the authors reported that atomic-scale graded structures were formed in alloys or compounds by the sedimentation of atoms, although a very high acceleration field of the order of 1 million grams was necessary.[5,6] At this time this method cannot be applied to glass because of temperature limits, and the size of the obtained graded materials is limited to a millimeter scale by the capacity of the ultracentrifuge machine. On the other side, the binary-oxide glasses had been prepared by sol−gel method in Si−Ti[7−11] and Si−Zr[12,13] systems and so forth. To achieve homogeneity of binary oxide gels, the sol−gel routes by hydrolysis/condensation,[7,8,10,13] prehydrolysis of the less reactive silicon alkoxide,[9,12] and nonhydrolytic reaction[11] had been used. Centrifugal processing was used to induce size selectrivity in Si particles suspended in a silica sol−gel precursor solution.[14] It is expected that in sol sedimentation colloid particles can easily occur under a comparatively low gravity field due to the large molecular weights.

In this study, we examined how to prepare molecular-scale graded oxide glasses in some binary systems (Si−Ti, Si−Zr, and Si−V) by combining the sol−gel method with centrifugal processing. The sol−gel treatment was done by hydrolysis/condensation. The characterizations were investigated by means of an electron probe micro-analyzer (EPMA), micro-area X-ray diffraction (XRD), and Fourier transform infrared (FT-IR) spectroscopy.

Experimental Procedure

Si−Ti Oxide System. The schematic representation of the preparation method is shown in Figure 1.[15] The t_A was increased to 18 h, and the total volume of ethanol was decreased to 2.55 mL (0.04376 mol) compared with the previous study. The t_B and t_C were 0.25 and 0 h, respectively. We set t_C very short (0 h) to set ultracentrifuge before the reaction.

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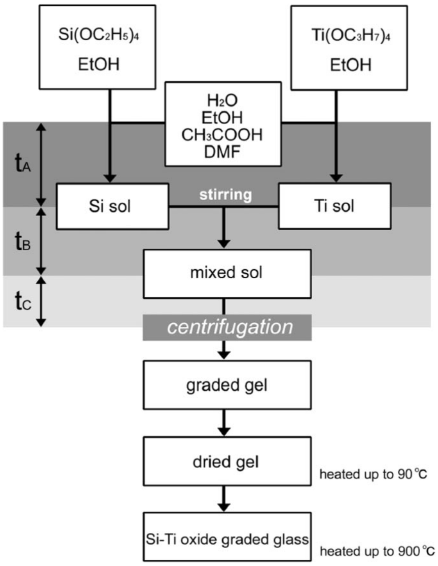

Figure 1. Preparation process of Si−Ti oxide graded glass.

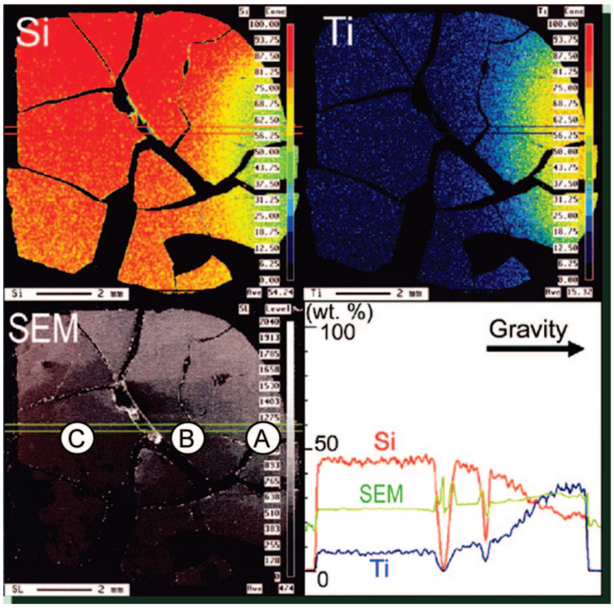

Figure 2. EPMA result of the Si−Ti oxide sample (Si:Ti = 85:15 (mol %); t_A−t_B−t_C = 18−0.25−0; maximum acceleration, 7500*g*; centrifuged time, 48 h).

The preparation procedure of the starting sol materials is as following. The 3.88 g (0.0186 mol) 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 1.36 g (0.0186 mol) of *N*,*N*-dimethylformamide (DMF: $(CH_3)NCHO$)] was 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 of 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 1.36 g (0.0186 mol) of DMF] was added to the Ti alkoxides solution under stirring.

Both the solutions were kept at 35−40 °C for homopolymerization for t_A (homopolymerization time) separately. After keeping for t_A at 35−40 °C, 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 ultracentrifuge experiments were undertaken by using a centrifugation machine (H-2000RF of Kokusan, Ltd.; maximum rotation, 12 000 rpm; maximum temperature, 80 °C). We have used the SH-2 rotor whose maximum radius in the sample from the rotation center was 140 mm. The mixed sol was put into a plastic tube with a diameter of 25 mm and a length

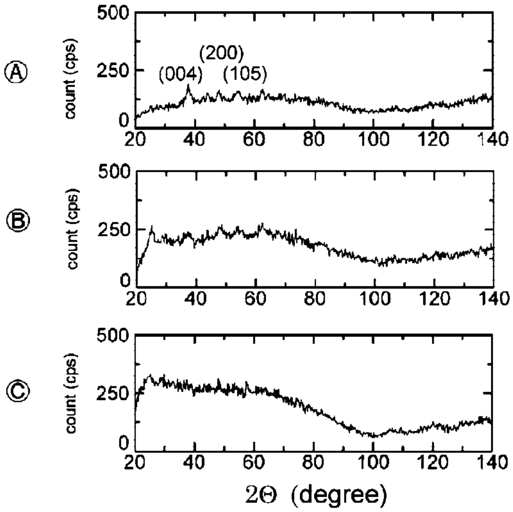

Figure 3. XRD patterns of Si−Ti oxide sample at the points A, B, and C in Figure 2.

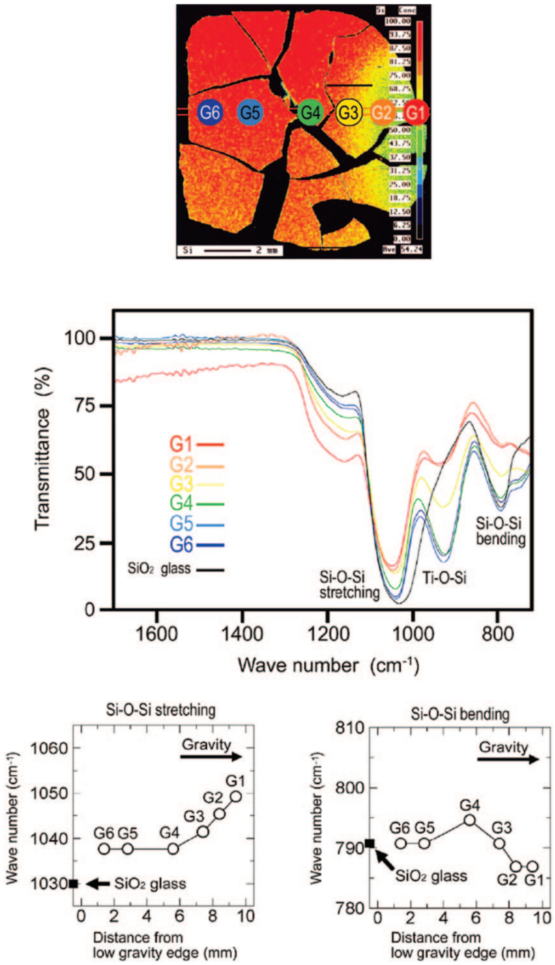

Figure 4. FT-IR spectra of Si−Ti oxide sample.

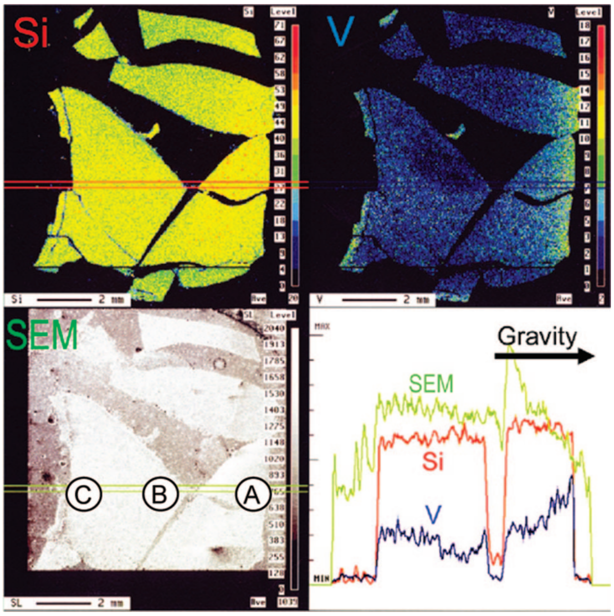

Figure 5. EPMA result of Si−V oxide sample (Si:V = 95:5 (mol %); $t_A-t_B-t_C = 13-0.25-0$; maximum acceleration, 15 000g; centrifuged time, 96 h).

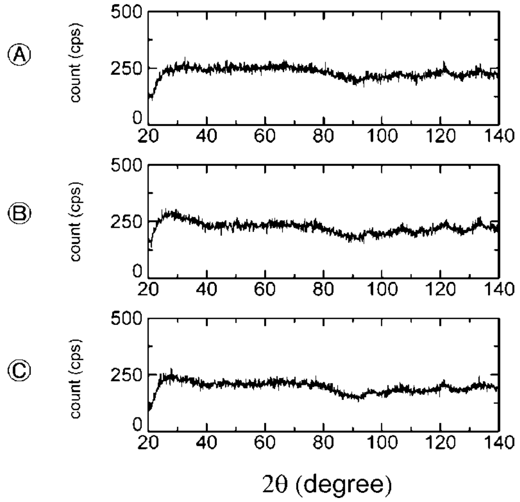

Figure 6. XRD patterns of Si−V oxide sample sample at the points A, B, and C in Figure 5.

of 105 mm, and set in the rotor. The samples were centrifuged by the rotation rate of 6900 rpm at about 40 °C for 48 h. The acceleration field at the top and bottom were calculated to be >6400 and 7500g, respectively. White gel with a size of 10 mm scale was obtained at the bottom of the plastic tube. Finally, the gel was dried at 90 °C to remove the solvent, and heated up to 900 °C to obtain the Si−Ti oxide glass. The obtained bulk specimen was analyzed by EPMA, XRD, and FT-IR.

Si−V Oxide System. The preparation procedure for the Si−V oxide system is also similar to the Si−Ti system. The t_A was 13 h, and the t_B and t_C were same as the case for Si−Ti. In this system, ethyl acetoacetate was contained in the catalyst solution for V alkoxide solution instead of the acetic acid. The 3.87 g (0.0186 mol) of tetraethoxysilane and 3.26 mL (0.0558 mol) of ethanol were stirred in a vial at room temperature. The catalyst solution [0.67 mL (0.0372 mol) of water, 3.26 mL of ethanol, 4.26 mL (0.0744 mol) of acetic acid, and the 1.36 g (0.0186 mol) of DMF] was added to the Si alkoxide solution under stirring for hydrolysis and polymerization. In another vial, 0.20 g (0.00098 mol) of vanadium (V) triethoxideoxide ($VO(OC_2H_5)_3$) and 0.34 mL of (0.00588 mol) ethanol were stirred, as well as Si alkoxide solution. The catalyst solution [0.03 mL (0.00147 mol) of water, 0.50 mL (0.00392 mol) of acetoacetate (EAA:$C_6H_{10}O_3$), and 0.07 mL (0.00098 mol) of DMF] was added to the V alkoxides solution under stirring.

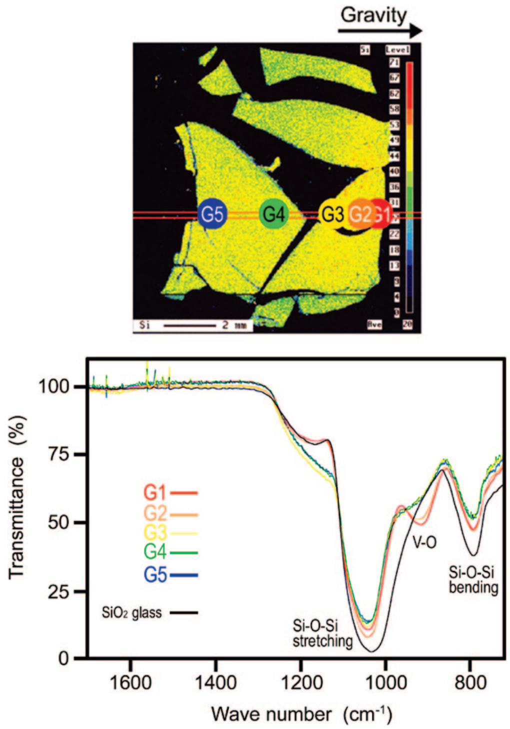

Figure 7. FT-IR spectra of the Si−V oxide sample.

The homopolymerization and mixing processes were same as the Si−Ti oxide system. The molar ratios of Si and V were 95:5 (mol %) in this system. The mixed sol was kept at t_C and was put into a plastic tube. The samples were centrifuged by the rotation rate of 8000 rpm at about 40 °C for 48 h. The acceleration field at the bottom was calculated to be 10 000g. White gel with a size of 10 mm scale was dried and heated by the same conditions as Si−Ti oxide system.

Si−Zr Oxide System. The preparation procedure for the Si−Zr system is also similar to that of the Si−Ti system. The t_A, t_B, and t_C were same as in the case of Si−V. In this system, ethyl acetoacetate was contained in the catalyst solution for Zr alkoxide solution instead of the acetic acid. The 1.93 g (0.00928 mol) of tetraethoxysilane and 2.71 mL (0.0464 mol) of ethanol were stirred in a vial at room temperature. The catalyst solution [0.33 mL (0.0186 mol) of water, 2.71 mL of ethanol, 2.13 mL (0.0371 mol) of acetic acid, and the 0.68 g (0.00928 mol) of DMF] was added to the Si alkoxide solution under stirring for hydrolysis and polymerization. In another vial, 0.19 g (0.00049 mol) of tetra-*n*-butoxy zirconium ($Zr(OC_4H_9)_4$) and 0.85 mL (0.0147 mol) of ethanol were stirred, as well as the Si alkoxide solution. The catalyst solution [0.07 mL (0.00392 mol) of water, 0.06 mL (0.00049 mol) of ethyl acetoacetate (EAA: $C_6H_{10}O_3$), and 0.03 g (0.00049 mol) of DMF] was added to the Zr alkoxides solution under stirring.

The homopolymerization and mixing processes were the same as the Si−Ti oxide system. The molar ratios of Si and Zr were 95:5 (mol %) in this system. The mixed sol was kept at t_C and was put into a plastic tube. The samples were centrifuged by the rotation rate of 9800 rpm at about 40 °C for 96 h. The acceleration field at the bottom was calculated to be 15 000g. White gel with a size of

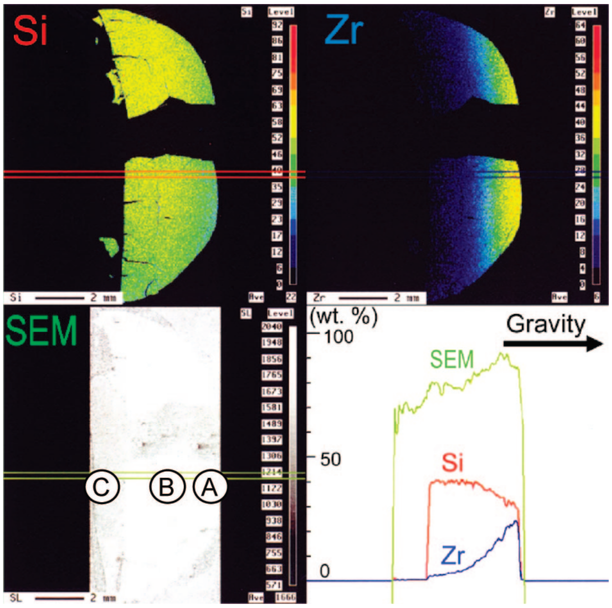

Figure 8. EPMA result of Si−Zr oxide sample (Si:Zr = 95:5 (mol %); $t_A-t_B-t_C = 13-0.25-0$; maximum acceleration, 15 000*g*; centrifuged time, 96 h).

10 mm scale was dried and heated by the same conditions as Si−Ti and Si−V oxide systems.

Results and Discussion

Si−Ti Oxide System. Figure 2 shows the EPMA photo-mapping with the linear composition profiles of Si and Ti at the polished surface in which plane contained the rotation axis of the Si−Ti oxide specimen that had some cracks. The obtained sample contained some cracks, but the number decreased compared with previous ones.[7] The concentration of Si continuously decreased, while that of Ti increased in the direction of the gravitational field. The change in composition or structure is due to not the difference in acceleration field but the sedimentation of the molecule, because the accelerations at the top and bottom part are not different. The XRD patterns at three points in Figure 2 are shown in Figure 3. The points A, B, and C correspond to the points of high, mid, and low gravity regions in the sample, respectively, indicated in Figure 1. All patterns consisted of a narrow peak (glass hump) in the low diffraction angle range. This showed that the specimen almost consisted of a graded glass structure, and the graded structure was continuous in molecular scale. However, we can see some small broad peaks of (004), (200), and (105) orientations and so forth of anatase-type TiO_2 in the patterns A and B in Figure 3. The grain sizes were estimated to be less than 10 nm by the Scherrer equation. This indicates that anatase-type TiO_2 nanosize crystals appear in the graded glass. In addition, the intensity of glass hump decreases from A to C. This may related to that the composition rate of TiO_2 decreasing to C, due to the large diffraction ability of Ti ions.

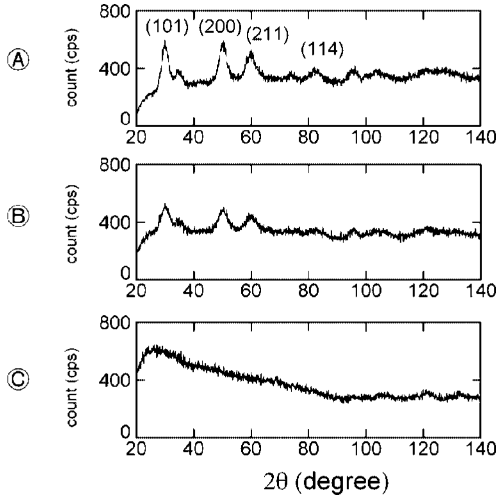

Figure 9. XRD patterns of Si−Zr oxide sample at the points A, B, and C in Figure 8.

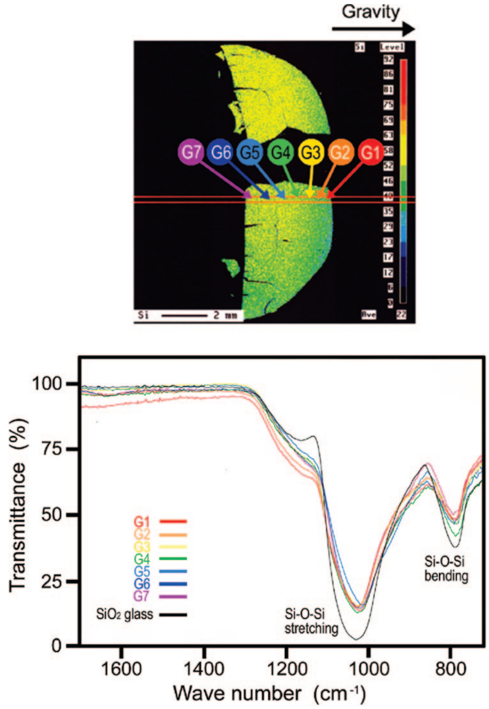

Figure 10. FT-IR spectra of the Si−Zr oxide sample.

The FT-IR result is shown in Figure 4. Absorptionbands around 800 cm^{-1} and 1040 cm^{-1} are assigned to Si−O−Si bending and Si−O−Si stretching, respectively.[16] The absorption band around 950 cm^{-1} could be attributed to the Ti−O−Si bond.[17,18] This shows that the SiO_2 and TiO_2 were mixed in molecular scale. The absorption peak of Si−O−Si stretching was shifted from about 1040 cm^{-1} to about 1050 cm^{-1}, while the absorption peak of Si−O−Si bending was shifted from about 790 cm^{-1} to about 780 cm^{-1} with the concentration of Ti. According to ref 19, the absorption frequencies for Si−O−Si stretching and bending decrease

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and increase, respectively, with the angle for Si−O−Si. We assumed that the angle of Si−O−Si bonds increased with the concentration of Ti because the distance between the Ti and the O atoms is longer than the distance between the Si and the O atoms.[19] The pressures by the acceleration field in the case of this experiment were very small (<3.3 MPa (0.033 kbar)), so we can ignore the pressure effect on vibrational peak positions (Si−O−Si).

Si−V Oxide System. Figure 5 shows the EPMA photomapping with the linear composition profiles of Si and V at the polished surface in which the plane contained the rotation axis of the Si−V oxide specimen that had some crack. The concentration of V increased, while the one of Si did not decrease much in the direction of the gravitational field. The XRD result that was measured in the specimen at three points is shown in Figure 6. All patterns consisted of a narrow peak in the low diffraction angle range, which only differed slightly in shape. This showed that the specimen had a graded glass structure, and the graded structure was continuously in molecular scale.

The FT-IR result is shown in Figure 7. Absorption band of the V−O−Si bond around 910 cm^{-1} appeared in the graded glass,[20] and the absorption rate increases with V. This indicates that the SiO_2 and VO_x were mixed in molecular scale. Absorption bands around 800 cm^{-1} (Si−O−Si bending) slightly decreased, and those around 1040 cm^{-1} (Si−O−Si stretching) slightly increased. These results also mean that the concentration of V increased in the direction of the gravitational field, because the distance of V−O is shorter than that of Si−O.

Si−Zr Oxide System. Figure 8 shows the EPMA photomapping with the linear composition profiles of Si and Zr at the polished surface in which the plane contained the rotation axis of the Si−Zr oxide specimen that had some crack. The concentration of Si continuously decreased, while that of Zr increased in the direction of the gravitational field. The XRD result that measured the specimen at three points is shown in Figure 9. The patterns A and B contained tetragonal ZrO_2 crystal broad peak[21] of (101), (200), and (211) orientations and so forth, while the pattern C consisted of only broad peaks in the low diffraction angle range, which showed the glass structure. The grain sizes of tetragonal crystal were estimated to be 1−5 nm by the Scherrer equation. This showed that the specimen contained the tetragonal ZrO_2 nanocrystals in the high gravity region. The FT-IR result is shown in Figure 10. The absorption bands assigned Si−O−Si bending and Si−O−Si stretching did not shift much, and the absorption band of the Zr−O bond was not observed. This result is consistent with that of the graded glass containing ZrO_2 nanocrystals in the high gravity region. This is reasonably understood by the generally accepted opinion that ZrO_2 does not easily form glass structure.[22]

Conclusion

We examined the preparation of graded composition structured oxide glasses in the Si−Ti, Si−V, and Si−Zr oxide systems by combining the sol−gel method with centrifugal processing. As a result, for the Si−Ti system, the molecular-scale graded oxide glass, where Si and Ti atoms located at the cation position in random-network glassy form, was prepared. The FT-IR spectroscopy result showed that infrared absorption peaks of Si−O−Si bending and stretching was shifted with increasing concentration of Ti. For the Si−V system, the molecular-scale graded glass was also prepared. For the Si−Zr oxide system, the graded composition glass which contained ZrO_2 nanocrystals in higher gravity area was prepared. The specimen size can be increased up to centimeter scale. Further study of physical properties is required for the application.

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