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Preparation of TiO_2–Na_2O glass by sol–gel method and structural characterization

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Abstract

The applicability of sol–gel process in glass formation of binary system, $(100 - x)TiO_2$–xNa_2O ($x = 10, 20, 30$), was investigated and the glasses were prepared successfully by the sol–gel process for the first time. The process of glass formation was checked by using X-ray diffraction measurement and DTA–TG analysis. In the baking step, a DTA peak related to the crystallization of gel was found. The short-range structure of glassified samples was studied by neutron scattering measurement. It is found from the results of neutron scattering measurement that the coordination number of O atom around Ti atom is about 4, and the O atoms around Ti atom form a planer square rather than a regular tetrahedron.

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1. Introduction

It is known that TiO_2 does not form glass by melt quenching. Therefore, Zachariasen [1] classified TiO_2 into intermediate oxide or network-modifying oxide. On the other hand, it is known that many binary and ternary titanates form glasses without any help of a network-forming oxide. So far, the binary glasses containing TiO_2, such as Cs_2O–TiO_2, Rb_2O–TiO_2, K_2O–TiO_2 [2], BaO–TiO_2 [3], Na_2O–TiO_2 [4], CaO–TiO_2 and SrO–TiO_2 [5], were prepared by melt quenching. Sakka et al. [6–8] reported that the binary glasses consisting of TiO_2 and alkali oxide were prepared by quenching the melts with a twin-roller. Their structural investigation by X-ray radial distribution analysis and Raman spectroscopic measurement showed that major portion of the Ti^{4+} ions were fourfold coordinated in the alkali-dititanate glasses, although considerable fraction of Ti^{4+} ions were sixfold coordinated in the $Na_2O \cdot 2TiO_2$ glasses compared with the $K_2O \cdot 2TiO_2$ and $Cs_2O \cdot 2TiO_2$ glasses.

Many glasses also can be prepared by sol–gel method. Because the sol–gel method can be performed at lower temperature compared to other methods, the various materials have been synthesized by the sol–gel method: for example, coating thin films [9,10], organic–inorganic hybrid [11,12], and so on. The sol–gel method expands to various fields besides the preparation of the glasses.

Sol–gel process of titanium oxide was investigated by Rivallin et al. [13]. And nanocrystallization of anatase in gel was reported by Švadlák et al. [14]. Trial of amorphisation of TiO_2 was reported in Refs. [15,16]. We traced their

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methods. However, when we heated the gel in order to remove organics after them, the samples were crystallized at about 300 °C. And amorphous material was not obtained. Hence we decided to make binary glasses containing TiO_2. Many binary glasses consisting of TiO_2 and network-forming oxide, such as SiO_2 and P_2O_5, were prepared by sol–gel method. However, as far as we know, there is no report that the binary glasses consisting of TiO_2 and network-modifying oxide, such as alkali oxide, were prepared by sol–gel method. It is very interesting to examine a possibility of the sol–gel method to prepare the binary titanate glasses. It is known that one of the crystalline forms of TiO_2, anatase, has the photocatalyst function, therefore TiO_2 is industrially interesting material.

In the present study, the sol–gel process in glass formation of TiO_2–Na_2O system was examined. The condition of glass formation was checked by X-ray diffraction measurement and DTA–TG analysis. The short-range structure of glassified sample prepared by sol–gel method was examined quantitatively by neutron scattering measurement.

2. Experimental procedures

2.1. Sample preparation

The glasses of $(100-x)TiO_2$–xNa_2O $(x = 10, 20, 30)$ system were prepared by the sol–gel method. An attempt of this method to make the TiO_2 glass was reported by Petkov et al. [15] and Wang et al. [16]. Petkov et al. used titanium tetraisopropoxide as starting material, while Wang et al. used titanium tetrabutoxide for preparing TiO_2 glass as well. After their methods, we used titanium tetraisopropoxide (Wako Chemicals Co. over 95%) and titanium tetrabutoxide (Wako Chemicals Co. over 95%) as the starting materials. The difference of the tendency of glassification and difference of structure between the two titanium alkoxides were examined. Sodium *t*-butoxide (Wako Chemicals Co. over 95%) also was used as the starting materials. The chemicals were used without further purification.

Fig. 1 shows a flow chart for preparation of the TiO_2–Na_2O glass. The details of the preparation for $80TiO_2$–$20Na_2O$ glass are as follows: (1) 0.5 mol of sodium *t*-butoxide was dissolved in 2.5 mol of ethanol; (2) after sodium *t*-butoxide was dissolved completely, 1 mol of titanium alkoxide (titanium tetraisopropoxide or titanium tetrabutoxide) was added in drops to this solution; (3) after titanium alkoxide was dissolved completely, the mixture of the 5 mol of water and the 2.5 mol of ethanol was added in drops to this solution; (4) this solution was kept at room temperature for a week, and afterwards, the filtration residue was dried for 1 h at 100 °C; (5) the obtained dried gel was baked for 1 h at 500 or 600 °C in order to remove residual organics.

In this paper, the samples are labeled by the kind of the used titanium alkoxide, the Na_2O content and the baking temperature. For example, the sample of $80TiO_2$–$20Na_2O$ made from titanium tetraisopropoxide baked at 600 °C is described as I20-600, where 'I' is the kind of titanium alkoxide, i.e. titanium tetraisopropoxide in this case, '20' is the Na_2O content, and '600' is the baking temperature. If titanium tetrabutoxide is used as starting material, 'B' is used in place of 'I'.

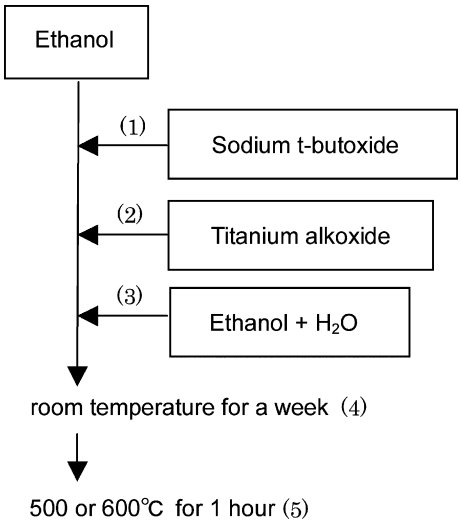

Fig. 1. Flow chart for preparation of the TiO_2–Na_2O glass by sol–gel process.

2.2. Measurements

X-ray diffraction measurement was carried out by using Geigerflex DXG1 X-ray diffractometer (Rigaku Co.) with Cu Kα radiation over $2\theta = 10$–$70°$ to check the glass formation of the sample. The glass forming process was elucidated by DTA–TG analysis with the apparatus of ThermoPlus2 TG8120 (Rigaku Co.). The heating rate was 10 °C/min.

The short-range structure of glassified sample was examined quantitatively by neutron scattering measurement by using high intensity total scattering spectrometer II (HIT-II) in high energy accelerator research organization (KEK). The samples were loaded in a vanadium metal cylinder with a wall thickness of 0.025 mm, an inner diameter of 8 mm and a length of 40 mm. The structure factor $S(Q)$ in Faber–Ziman definition [17] was obtained from the measured scattering intensity after some corrections, such as subtraction of cell intensity, correction of absorption, subtraction of multiple scattering intensity, normalization with scattering intensity from vanadium standard, and so on. These correction procedures have been reported in detail elsewhere [18,19].

3. Results

3.1. X-ray diffraction measurement

Fig. 2 shows X-ray powder diffraction spectra of the samples made from titanium tetraisopropoxide. For