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Full Length Article

Formation of nonlinear optical $Na_2TeW_2O_9$ crystals and laser irradiation in tungsten–tellurite glasses

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ABSTRACT

The crystallization behavior of $25Na_2O–50WO_3–25TeO_2$ glass was examined to develop transparent glass-ceramics containing nonlinear optical $Na_2TeW_2O_9$ crystals. It was clarified from XRD analysis and Raman scattering spectra that a metastable crystalline phase is formed initially and the stable crystalline phase of $Na_2TeW_2O_9$ is created through the transformation of the metastable phase. Laser irradiations (continuous wave Yb:YVO_4 fiber laser, wavelength of 1080 nm) with the condition of the laser power of $P = 0.55$ W and scanning speed of $S = 2.3$ μm/s created the patterning of homogeneous crystals lines. The crystalline phase in the laser irradiated part was proposed to be the metastable crystalline phase from micro-Raman scattering spectra.

1. Introduction

Tellurium oxide (TeO_2)-based glasses are of scientific and technological interest on account of their low melting temperature, high refractive index, high dielectric constant, high infrared transmission, and low phonon energy (good host for RE ions). The structure of TeO_2-based glasses is also of interest, because there are two types of basic structural units, i.e., TeO_4 trigonal bipyramid (tbp) and TeO_3 trigonal pyramid (tp). So far, many binary and ternary glasses such as $ZnO–TeO_2$ and $K_2O–WO_3–TeO_2$ have been synthesized, and for example, it is known that the system of $Na_2O–ZnO–TeO_2$ with rare-earth ions is a good candidate for optical amplifier glasses [1]. Crystallization of glasses is a method for fabrication of transparent and dense condensed materials with desired shapes and functions, and so far, various functional glass-ceramics have been proposed through the design and control of glass composition, nucleation and crystal growth [2–5]. It is, therefore, of interest to develop transparent TeO_2-based crystallized glasses (glass-ceramics), and this topic is regarded as frontiers in the glass science and technology because of limited reports on the crystallization of TeO_2-based glasses. For example, transparent crystallized glasses exhibiting a second harmonic generation (SHG) have been fabricated in the glass with the composition of $15K_2O–15Nb_2O_5–70TeO_2$ [6–14]. The crystallization behavior of $BaO–RE_2O_3–TeO_2$ glasses (RE: La, Pr, Sm, Eu, Er) has been also examined, and transparent crystallized glasses with fluorite-type $RE_2Te_6O_{15}$ or $RE_2Te_5O_{13}$ nanocrystals (~50 nm sizes) were successfully fabricated [15–17].

The $Na_2TeW_2O_9$ crystalline phase is known to be a non-centrosymmetric tellurite with a polar monoclinic space group *Ia* (No. 9) and exhibits a strong SHG of the effective nonlinear coefficient $d_{eff} = 6.9$ pm/V [18–21]. Its three-dimensional structure consists of corner-sharing layers of WO_6 octahedra that are connected with asymmetric Te^{4+} cations. On the other hand, it is known that the $Na_2O–WO_3–TeO_2$ system shows a wide glass-forming region [22,23], and it is suggested that WO_3 acts as a network former in the structure [23]. It is, therefore, of interest to study the crystallization behavior of $Na_2O–WO_3–TeO_2$ glasses and to fabricate transparent crystallized glasses consisting of $Na_2TeW_2O_9$ crystals. So far, the crystallization of $Na_2O–WO_3–TeO_2$ glasses has not been reported.

The purpose of this study is to clarify the crystallization behavior of $25Na_2O–50WO_3–25TeO_2$ glass in order to develop new transparent TeO_2-based crystallized glasses showing SHG. In particular, we focus our attention on whether nonlinear optical $Na_2TeW_2O_9$ crystals are formed directly in the crystallization of glasses or whether a metastable crystalline phase is formed initially and transforms into the stable $Na_2TeW_2O_9$ crystalline phase. The present study will provide a more deep and general understanding for the crystallization

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of TeO_2-based glasses. The laser patterning of crystal lines is also tried.

2. Experimental

The chemical composition in the Na_2O–WO_3–TeO_2 system studied in the present study is $25Na_2O$–$50WO_3$–$25TeO_2$, which corresponds to that of nonlinear optical $Na_2TeW_2O_9$ crystal. Glasses were prepared using a conventional melt quenching method. Commercial powders of reagent grade Na_2CO_3, WO_3, and TeO_2 were mixed and melted in a platinum crucible at 800 °C for 30 min in an electric furnace. In the present study, any chemical analysis for the samples prepared has not been carried out, and we use the nominal composition through this paper. Melts were poured onto an iron plate and pressed to a thickness of ~1.5 mm with another iron plate. The glass transition, T_g, and crystallization peak, T_p, temperatures were determined using differential thermal analyses (DTA) at a heating rate of 10 K/min. Densities of the glasses were determined by the Archimedes method using distilled water as the immersion liquid.

The glasses were mechanically polished to a mirror finish with CeO_2 powders, and heat-treated at different temperatures. The crystalline phases present in heat-treated samples were examined from X-ray diffraction (XRD) analyses at room temperature by using Cu $K\alpha$ radiation, in which both plate bulk samples and powdered samples (i.e., bulk crystallized samples were pulverized by using an agate mortar: particle size: <20 μm) were used. The crystalline phase was also examined from micro-Raman scattering spectrum measurements (Tokyo Instruments Co., Nanofinder; Ar^+ laser λ = 488 nm). SHG microscopic measurements were performed for the crystallized samples using a Q-switched Nd:YAG (yttrium aluminum garnet) laser with λ = 1064 nm as a fundamental light source [24].

A glass with a small amount (0.5 mol%) of CuO, $0.5CuO$–$25Na_2O$–$50WO_3$–$25TeO_2$, was irradiated by cw Yb:YVO_4 fiber laser (beam shape: single mode and ±1 nm bandwidth) with λ = 1080 nm using objective lens (magnification: 50 times, numerical aperture: NA = 0.8). The laser beam was unpolarized and the diameter of laser spot was 2–3 μm. Plate-shaped glasses with a thickness of ~1 mm were put on the stage and mechanically moved during laser irradiations to pattern crystals. Different laser powers (P) of P = 0.5–0.6 W and laser scanning speeds (S) such as S = 2–3 μm/s were used. The morphology and crystalline phase in the laser-irradiated part were examined from polarized optical microscope (POM) observations (Olympus-BX51) and micro-Raman scattering spectrum measurements.

3. Results and discussion

3.1. Thermal properties and crystallization behavior

The glass of $25Na_2O$–$50WO_3$–$25TeO_2$ is designated here as NaWTeO glass. The melt-quenched NaWTeO sample is optically transparent, and the amorphous state was confirmed from XRD analysis. The density of NaWTeO glass was 5.796 g/cm^3. The DTA patterns at a heating rate of 10 K/min in air for the melt-quenched samples are shown in Fig. 1. Both samples of bulk and powder shapes have similar DTA patterns, showing the values of T_g = 367–368 °C and T_p = 431–432 °C and thus suggesting the mechanism of bulk crystallization. Furthermore, the appearance of three exothermic peaks suggests that the crystallization behavior is not simple.

The XRD patterns at room temperature for the samples heat-treated at 420, 460, 480, 500, and 580 °C for 1 h are shown in Figs. 2 and 3, in which the bulk plates were pulverized after heat treatments. The peaks observed in these heat-treated samples are not assigned to the nonlinear optical $Na_2TeW_2O_9$ crystalline phase being a target crystalline phase in this study. It is considered from XRD patterns that only one crystalline phase is formed in the heat treatment temperatures of 420–580 °C. As seen in Fig. 1, these temperatures of 420–580 °C are lower than the temperature of T_{p3} = 614 °C. At this moment, the crystalline phase indicated in Figs. 2 and 3 has not been identified, i.e., the unidentified phase. It should be pointed out that the samples heat-treated at 420 and

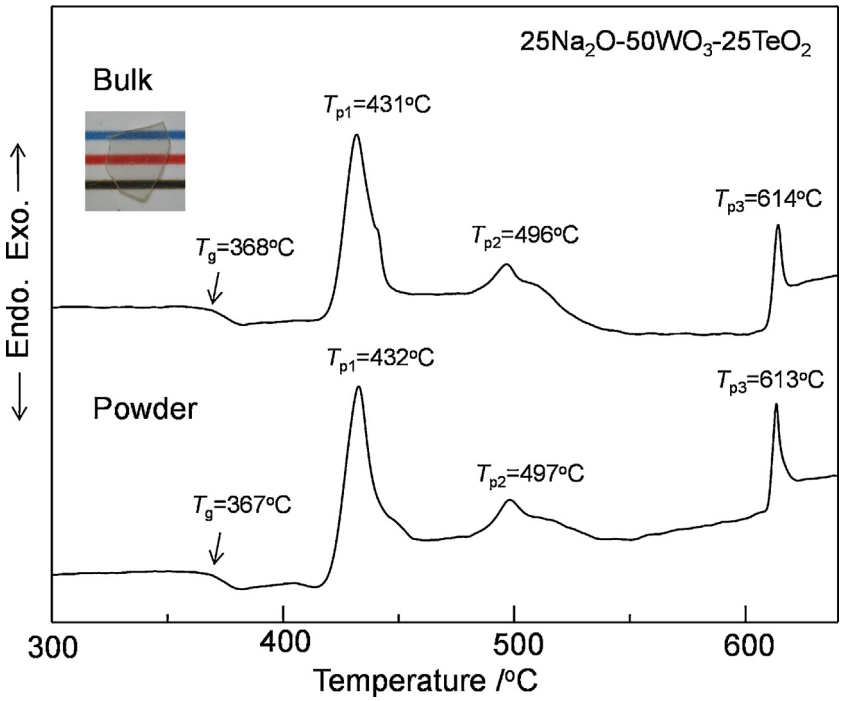

Fig. 1. DTA patterns for the bulk and powder samples of $25Na_2O$–$50WO_3$–$25TeO_2$ glass. Heating rate was 10 K/min. The optical photograph for the as-quenched sample is included.

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