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Effect of annealing in an H_2 gas atmosphere on the physical properties for $70V_2O_5 \cdot 30TeO_2$ (mol%) glasses

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ABSTRACT

Powdered $70V_2O_5 \cdot 30TeO_2$ (mol%) glasses were annealed in an H_2 gas atmosphere at 473 K for 1 h and 2 h, respectively. The difference between their physical properties before and after annealing was investigated. The mass of the powders decreased with an increase in the annealing time. Glass transition temperature (Tg) was 512 ± 0.1–513 ± 0.1 K for the annealed powders, indicating that the Tg values became lower than the as-quenched glass powder (Tg = 517 ± 0.1 K). The fraction of reduced vanadium ion ($Cv = V^{4+} / (V^{4+} + V^{5+})$) increased with an increase in the annealing time: Cv = 0.020 ± 0.003, 0.024 ± 0.003 and 0.0272 ± 0.0033. From IR observation, it was determined that the glass structure in the annealed glasses ultimately incorporated a much larger amount of TeO_3 trigonal pyramid units compared with the as-quenched glass powder. It was determined that the DC electrical conductivity (σ) of the pelletized powders, which were n-type semiconducting, depended on the annealing time of the powders. The largest σ was (5.78 ± 0.28) × 10^{-5} S cm^{-1} at 473 K for the pellet of the powder annealed for 2 h. The activation energy for electron hopping (W) was determined to be 0.380 ± 0.0005–0.420 eV ± 0.0005 eV, indicating that W decreased with an increase in the annealing time. The annealing contributed to the release of O from the glasses by changing the unit in the glasses from the TeO_4 to TeO_3: $TeO_4 + H_2 \rightarrow TeO_3 + H_2O\uparrow$.

1. Introduction

Electrical-conductive glasses containing vanadium oxide have been widely studied for their electrical properties [1–11]. The DC electrical conductivity (σ) of these glasses was found to be 10^{-7}–10^{-2} S cm^{-1} [1 − 11]. The conducting behavior of the glasses arises due to the hopping of electrons from lower to higher valence state: $V^{4+} - O - V^{5+} \rightarrow V^{5+} - O - V^{4+}$ [1–3,5–10]. The electrical application of this hopping process was also studied. Among these glasses, those with $\sigma = 10^{-5}$–10^{-3} S cm^{-1} at 473 K were reported to have potential applicability for use in electrical devices (e.g., memory switching [12] and oxygen gas sensors [13,14]). The sensing mechanism was attributed to a $V^{4+} \rightarrow V^{5+}$ change produced by oxygen which had diffused in to the glasses from the oxygen atmosphere, resulting in decrease in the σ [13,14]. Recently, the thermal and structural characteristics of V_2O_5-P_2O_5-TeO_2 glasses were studied for the application of lead-free low-temperature sealing [15]. The electrical conduction mechanism for the vanadate glasses was investigated by using small polaron hopping and variable range hopping models [16–18], Schnakenberg's model [19] and Shimakawa's multiphonon tunneling model [20].

A melt quenching method was used for the preparation of the glasses [3–11]. After preparation by the melt quenching method, the glasses were annealed [21,22] or crystallized [10,23,24] to form a closely packed structure in the glasses compared with that of the as-quenched glasses [23]. Ultimately, the glasses resulted in a very high σ value. The atmosphere in the furnace during the melting and annealing was air [4–6] or Ar gas [8].

For preparation of particles [25] and thin films [26,27], an hydrogen annealing process was used and effect of the atmosphere for these materials was investigated. From these investigations, changes of crystal structure [25,26] and O—H bonding formation [27] were confirmed. In this work, this annealing process was applied to prepare vanadium tellurite binary glasses. For vanadium tellurite binary glasses containing V_2O_5 of more than 35 mol%, it was confirmed that Te in the glasses was 4- and 3-coordinated [28]. Thus, two different effects from the annealing were expected to result: First, a change in the structure of the tellurite oxides and second, an increase in the concentration of V^{4+}. These effects can be expressed by the following chemical reactions, respectively:

$$TeO_4 + H_2 \rightarrow TeO_3 + H_2O\uparrow \quad (1)$$

$$V_2O_5 + H_2 \rightarrow 2VO_2 + H_2O\uparrow \quad (2)$$

Eq. (1) suggests the decrease of O ions that are an obstacle to the hopping of electrons between vanadium ions. Eq. (2) suggests an increase in the carrier density. The purposes of the present study were

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Table 1
Annealing condition for the powders of $70V_2O_5 \cdot 30TeO_2$ glasses (mol%).

Sample name	Time (h)	Temperature (K)	Atmosphere
H2-0h	0	–	–
H2-1h	1	473	H_2
H2-2h	2	473	H_2

two fold. The first purpose of the study was to clarify the difference between physical properties (mass, glass transition and crystallized temperatures (*Tg* and *Tc*), density, the fraction of reduced vanadium ion (*Cv*) and σ) before and after annealing. The second purpose was to observe the infrared absorption spectra of the glasses and to investigate their glass structures. Regarding the above reactions, the as-quenched glasses were powdered in order to easily react with the H_2. Based on the obtained results, the author will discuss the above effects further on in this paper.

2. Method

2.1. Preparation of powdered glass samples

The samples used for the experiment were $70V_2O_5 \cdot 30TeO_2$ (mol%), and this was the largest amount of V_2O_5 among the vanadium tellurite binary glasses prepared in our previous work [5,6,8]. Reagent-grade V_2O_5 (99.9% purity, Furuuchi chemical) and TeO_2 (99.99% purity, Furuuchi chemical) were used as raw materials. The components in the prescribed composition were mixed in air, and a batch was melted in an alumina crucible in air in an electric furnace at 1023 K for 1 h. The melts were quenched by using copper plates. For each sample glass powder, the bulk glasses of 5 g in mass were crushed in air. Three powdered samples were then prepared. Among these, two samples were annealed in the H_2 atmosphere. Table 1 shows the annealing conditions for the glass powders. One of the samples was annealed at 473 K for 1 h (sample name: "H2-1h"), and the other sample was annealed at 473 K for 2 h (sample name: "H2-2h"). The masses of the samples were measured before and after annealing. The name of the as-quenched glass powder was "H2-0 h".

2.2. Analysis of physical properties for the powder samples

The amorphous nature of the samples was confirmed by X-ray diffraction (XRD) using a Philips X'Pert MPD diffractometer. Particle sizes of each sample were measured by optical microscopic observation. The *Tg* and *Tc* were analyzed using a TA Instrument DSCQ100 at a heating rate 10 K min^{-1} in a N_2 gas atmosphere. The V^{4+} ion concentration and total vanadium ion concentration ($V^{4+} + V^{5+}$) were determined by titration using $KMnO_4$ and $FeSO_4(NH_4)SO_4$ solutions. Afterwards, the fraction of reduced vanadium ion (*Cv*, and defined on $Cv = V^{4+} / (V^{4+} + V^{5+})$) was obtained. IR absorption spectra at room temperature for the samples were recorded by a KBr tablet method with JEOL WINSPEC-100 spectrometer. In addition, the spectrum of a TeO_3, which was reagent-grade raw material (99.9% purity, Kojundo Chemical Laboratory Co, Ltd), was also observed for use as a contrastive analysis.

2.3. Preparation of pelletized glasses and analysis of electrical property

For each sample, a pellet was prepared by pressing the powder (approximately 1 g) at 160 MPa in air. Fig. 1 shows a photograph of the one of pellets (this photograph is the pelletized powder annealed at 473 K for 2 h). The diameter and thickness of the pellets were measured by using a micrometer (Mitsutoyo Co.). The density was determined by using the measured values of mass, diameter and thickness. The four-point probe method was employed to determine the σ at 303–473 K, where 1.0 μA direct current was applied during the measurement.

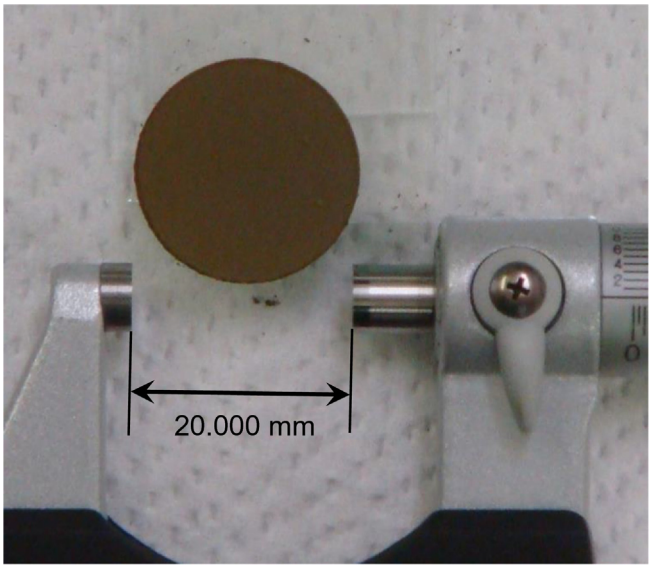

Fig. 1. Photograph of the pelletized powder annealed at 473 K for 2 h.

Electrodes were made with a platinum paste. Thermoelectric power was measured by keeping a temperature difference of 5–10 K between the two surfaces for each pellet. DC polarization due to ionic current was confirmed from the results of the relationship between voltage and its measuring time at 453, 463 and 473 K. Direct currents of 0.1, 1.0, 10 and 100 μA were applied for the polarization measurements. In addition, ohmic contact between the paste and pellets was confirmed from the results of the voltage-current relation. The voltage and temperature were recorded using Graphtec midi LOGGER (GL 200A), respectively.

3. Results

3.1. Physical properties of the powders before and after annealing

From the optical microscopic observation, the particle size was confirmed to be within 100 μm for all samples. No peaks due to vanadium oxides or tellurite oxides were found from XRD analysis for the powders before and after annealing which characterized the amorphous nature of the powders. Table 2 shows the physical properties of the powders. The masses of "H2-1h" before and after the annealing process were 4.9802 ± 0.00005 g and 4.9687 ± 0.00005 g, respectively. The mass decreased at the rate of 0.2309% [i.e., (4.9802 − 4.9687) / 4.9802 × 100]. For "H2-2h", the mass before annealing was 5.1038 ± 0.00005 g. After annealing, the value was 5.0678 ± 0.00005 g, indicating that the rate was 0.7050% [i.e., (5.1038 − 5.0678) / 5.1038 × 100]. The *Tg* and *Tc* were *Tg* = (512–517) ± 0.1 K and *Tc* = (557–558) ± 0.1 K. The results of the chemical analysis by titration are summarized in Table 3. The mass of V^{4+} ion in each powder with a mass of 1 g was V^{4+} = 0.0080 ± 0.0013 g, 0.0093 ± 0.0013 g and 0.0107 ± 0.0013 g. The value increased with an increase in the annealing time. The mass of $V^{4+} + V^{5+}$ was 0.3973 ± 0.0009 g, 0.3944 ± 0.0009 g and 0.3932 ± 0.0009 g for "H2-0 h", "H2-1h" and "H2-2h", respectively; the *Cv* was 0.020 ± 0.003, 0.024 ± 0.003 and 0.272 ± 0.0033, and the analytical concentration of V_2O_5 was 73.55 ± 0.06 mol%, 73.05 ± 0.06 mol% and 72.85 ± 0.06 mol%, respectively.

Fig. 2 shows the results of IR spectroscopic observation. The observed IR absorption bands for each sample are summarized in Table 4. The bands at 424–430, 460, 498–511, 665–661, 680–682, 766–769, 808–810, 890 and 974–977 cm^{-1} were confirmed to appear. In addition, bands at 426, 450, 492 and 692 cm^{-1} were observed for the TeO_3.