Thermal Stabilities, Physical and Optical Properties of K$_2$O-Na$_2$O-Nb$_2$O$_5$-TeO$_2$ Glasses


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Abstract: The thermal stabilities, physical and optical properties of xK$_2$O-(14-x)Na$_2$O-14Nb$_2$O$_5$-72TeO$_2$ (x = 0 ∼ 12 mol%) glasses have been studied. The glasses consisting of ca. 10 mol% K$_2$O show high thermal stabilities with values of $\Delta T = T_x - T_g = \text{ca. } 10^5 \degree C$ against crystallization, where $T_g$ and $T_x$ are the glass transition and crystallization onset temperatures, respectively. The activation energy of grain growth of a cubic crystalline phase in the 10K$_2$O-4Na$_2$O-14Nb$_2$O$_5$-72TeO$_2$ glass was 7.92 kJ/mol. The energy required for the phase transformation from the 10K$_2$O-4Na$_2$O-14Nb$_2$O$_5$-72TeO$_2$ glass to the cubic crystalline phase was 190.74 kJ/mol. The optical and physical properties of the K$_2$O-Na$_2$O-Nb$_2$O$_5$-TeO$_2$ glasses were obtained: refractive index, $n = 1.88$-$1.97$; $\rho = 4.22$-$4.64$ g/cm$^3$; optical energy band of the transmission cut-off wavelength, $E_g$ (eV) = 3.17-3.14; relative permittivity, $\varepsilon_r = 28$-$29$. The values of $R_M$ and $\alpha_m$ for K$_2$O-Na$_2$O-Nb$_2$O$_5$-TeO$_2$ glasses were much larger than those of Na$_2$O-Nb$_2$O$_5$-TeO$_2$ glasses.

Keywords: TeO$_2$ glasses, refractive index, molar volume, thermal stability, activation energy

Introduction

Tellurium oxide-based glasses are of scientific and technical interest on account of their low melting temperatures [1,2], large thermal expansion [3], high refractive indices, high dielectric constants, and good infrared transmissions; thus, recently they have been considered as promising materials for use in optical fibers and nonlinear optical devices [4-8]. Furthermore, the structures of TeO$_2$-based glasses have frequently been examined using Raman and IR spectroscopy. There are two types of basic structural units: TeO$_4$ trigonal bipyramids (tbp) with two equatorial and two axial Te-O bonds and a lone pair of electrons located on the third equatorial site, and TeO$_3$ trigonal bipyramids (tp) [9,10]. In these structures, the coordination circumstance of Te changes from TeO$_4$ to TeO$_3$ upon increasing the alkali metal ion content or raising the temperature [11]. Recently, our group [12-14] succeeded in fabricating transparent glass-ceramics from the system K$_2$O-Nb$_2$O$_5$-TeO$_2$ and discovered that the crystallized glasses exhibited second harmonic generation (SHG). Tanaka and coworkers [15] observed SHG in electrically poled Li$_2$O-Nb$_2$O$_5$-TeO$_2$ and Nb$_2$O$_5$-TeO$_2$ glasses. Yoko and coworkers [16] measured the third-order nonlinear optical susceptibilities, $\chi^{(3)}$, of various TeO$_2$-based glasses containing transition metal oxides and reported that the 30NbO$_{2.5}$-70TeO$_2$ glass shows a very large value of $\chi^{(3)}$. These previous studies indicate that not only TeO$_2$-based glasses but also their glass-ceramics have high potential for use as new optical functional materials. Very recently, we succeeded in fabricating transparent K$_2$O-Na$_2$O-Nb$_2$O$_5$-TeO$_2$ glassceramics and discovered [17] that some of them exhibit SHG. A slight distortion from the cubic structure in the crystalline phase formed in TeO$_2$-based glass-ceramics had

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Thermal Stabilities, Physical and Optical Properties of K2O-Na2O-Nb2O5-TeO2 Glasses

Table 1. Values of Glass Transition, Tg, Crystallization Onset, Tx, and Melting, Tm, Temperatures and Wavelength at the Absorption Edge, λab, for xK2O-(14-x)Na2O-14Nb2O5-72TeO2 Glasses (x = 0 ∼ 14 mol%)

<table>
<thead>
<tr>
<th>x (mol%)</th>
<th>Tg (°C)</th>
<th>Tx(°C)</th>
<th>Tm(°C)</th>
<th>λab(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>341</td>
<td>409</td>
<td>672</td>
<td>390</td>
</tr>
<tr>
<td>2</td>
<td>346</td>
<td>411</td>
<td>688</td>
<td>392</td>
</tr>
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<td>4</td>
<td>349</td>
<td>416</td>
<td>693</td>
<td>392</td>
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<td>6</td>
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<td>8</td>
<td>359</td>
<td>437</td>
<td>705</td>
<td>394</td>
</tr>
<tr>
<td>10</td>
<td>366</td>
<td>468</td>
<td>701</td>
<td>393</td>
</tr>
<tr>
<td>12</td>
<td>370</td>
<td>470</td>
<td>703</td>
<td>394</td>
</tr>
</tbody>
</table>

been proposed, which leads to SHG. To develop TeO2-based glasses or transparent glass-ceramics for use as nonlinear optical materials, an understanding of the thermal stability, electronic, physical, and optical properties is necessary, but such information is lacking when compared with studies on the structural or optical properties.

The purpose of this study was to examine the thermal stability and electronic, physical, and optical properties of K2O-Na2O-Nb2O5-TeO2 glasses whose glass-ceramics show SHG. The kinetics of formation of a cubic crystalline phase in K2O-Na2O-Nb2O5-TeO2 glasses were investigated and obtained from differential thermal analysis (DTA).

Experimental

Glasses in the series xK2O-(14-x)Na2O-14Nb2O5-72TeO2 (x = 0 ∼ 12 mol%) were prepared using a conventional melt-quenching method. Commercial powders of K2CO3 (99.5 %, Nacalai Tesque), Na2CO3 (99.5 %, Soekawa Chemicals), Nb2O5 (99.9 %, Soekawa Chemicals), and TeO2 (99 %, Soekawa Chemicals) were mixed and melted in a platinum crucible at 1000 °C for 40 min in an electric furnace. The batch weight was 15 g. The liquids were poured onto a carbon plate heated at 250 °C.

The glass transition, Tg, crystallization peak, Tx, temperatures were determined using DTA [18] at a heating rate of 10 Kmin⁻¹. The glassy state in the quenched samples and the crystalline phase present in the heat-treated samples were characterized by X-ray diffraction (XRD) analysis at room temperature using CuKα radiation [19,20]. The densities of the glasses and heat-treated samples were determined using the Archimedes method with ethanol as the immersion liquid. The refractive indices at a wavelength of 632.8 nm (He-Ne laser) were measured at room temperature using an ellipsometer (Mizojiri Optical Co., DVA-36 L model). The relative permittivities, εr, at a frequency of 10 kHz were measured using an LCR meter (AG-4311B, Ando Electric Co.) in the temperature range from room temperature to ca. 200 °C. Ion-sputtered gold films were used as electrodes for the measurement of εr. DTA was conducted in the temperature range 30 ∼ 1000 °C with various heating rates (10, 20, 25, and 30 °C/min).

Results and Discussion

The DTA curve of the 14Na2O-14Nb2O5-72TeO2 glass is shown in Figure 1 as an example. The values of the glass transition, Tg, crystallization onset, Tx, and melting, Tm, temperatures were 341, 409, and 672 °C, respectively. The values of Tg, Tx, and Tm for xK2O-(14-x)Na2O-14Nb2O5-72TeO2 (x = 0 ∼ 12) glasses, which were determined from DTA curves, are given in Table 1. In xK2O-(14-x)Na2O-14Nb2O5-72TeO2 (x = 0 ∼ 12) glasses, the values of Tg (341 ∼ 370 °C) and Tm (409 ∼ 470 °C) increased monotonously upon increasing the K2O/Na2O ratio. If we use the difference between Tg and Tx, ΔT = Tx - Tg, as an indicator of the thermal stability, it is obvious that the thermally stable glasses in the xK2O-(14-x)Na2O-14Nb2O5-72TeO2 series were obtained for the glasses having x = 10 ∼ 12. For example, large values of ΔT (102 °C) were obtained for the glasses with x = 10 ∼ 12. Thus, the 10K2O-4Na2O-14Nb2O5-72TeO2 glass exhibited high thermal stability against crystallization.

The room-temperature optical absorption spectra for xK2O-(14-x)Na2O-14Nb2O5-72TeO2 glasses are shown in Figure 2. The wavelength at the absorption edge, λab,
Table 2. Values of Molar Refractivity, \( R_M \), and Polarizability, \( \alpha_m \), for xK\(_2\)O-(14-x)Na\(_2\)O-14Nb\(_2\)O\(_5\)-72TeO\(_2\) Glasses (x = 0\(\sim\)14 mol%)

<table>
<thead>
<tr>
<th>x (mole%)</th>
<th>( R_M ) (cm(^3)/mol)</th>
<th>( \alpha_m ) ((\times)10(^{-24}) cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>17.45</td>
<td>6.91</td>
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<td>2</td>
<td>17.47</td>
<td>6.92</td>
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<td>4</td>
<td>18.06</td>
<td>7.15</td>
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<td>6</td>
<td>18.22</td>
<td>7.21</td>
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<tr>
<td>8</td>
<td>18.52</td>
<td>7.33</td>
</tr>
<tr>
<td>10</td>
<td>18.68</td>
<td>7.41</td>
</tr>
<tr>
<td>12</td>
<td>18.88</td>
<td>7.48</td>
</tr>
</tbody>
</table>

Figure 2. Optical absorption spectra recorded at room temperature for TeO\(_2\)-based glasses.

was determined by drawing a tangent (as shown by the dotted line in Figure 2) to the vertical edge that gives an intercept on the wavelength axis. In xK\(_2\)O-(14-x)Na\(_2\)O-14Nb\(_2\)O\(_5\)-72TeO\(_2\) glasses, the value of \( \lambda_{ab} \) remained almost constant irrespective of the K\(_2\)O/Na\(_2\)O ratio. The obtained values are given in Table 1.

The relationship between the density (\( \rho \)), and refractive index (n) is shown in Figure 3. In xK\(_2\)O-(14-x)Na\(_2\)O-14Nb\(_2\)O\(_5\)-72TeO\(_2\) glasses, both \( \rho \) (4.22\(\sim\)4.64 g/cm\(^3\)) and n (1.88\(\sim\)1.97) increased gradually upon increasing the K\(_2\)O/Na\(_2\)O ratio. The obtained values are shown in Figure 3.

The relationship between the refractive index and density of a material can be expressed using the well-known Lorentz-Lorentz formula [21,22],

\[
\frac{(n^2-1)}{(n^2+2)} \left( \frac{M_w}{\rho} \right) = R_M
\]

where \( M_w \) is the molecular weight of the material and \( R_M \) is the molar refraction. Further, the molar refraction depends on the polarizability, \( \alpha_m \), of the material, expressed by

\[
\alpha_m = 3 \cdot R_M / 4 \pi N
\]

where \( N \) is Avogadro’s number. The values of \( R_M \) and \( \alpha_m \) of the glasses were evaluated using equations (1) and (2), respectively.
Thermal Stabilities, Physical and Optical Properties of K₂O-Na₂O-Nb₂O₅-TeO₂ Glasses

Figure 4. Molar volumes, V_m, of xK₂O-(14-x)Na₂O-14Nb₂O₅-72TeO₂ and xNa₂O-(28-x)Nb₂O₅-72TeO₂. The solid straight lines were obtained by least-squares fitting.

Figure 5. Temperature dependence of the relative permittivity for TeO₂-based glasses. The frequency was 10 kHz. The lines are drawn as a guide for the eye.

Figure 6. Powder XRD patterns recorded at room temperature for heat-treated samples of xK₂O-(14-x)Na₂O-14Nb₂O₅-72TeO₂ glasses: (A) x = 0 mol%, (B) x = 6 mol%, (C) x = 8 mol%, (D) x = 10 mol%, and (E) x = 14 mol%.

they are given in Table 2. The values of Rₓₐ (17.45 ∼ 18.88 cm mol⁻¹) and aₚ (6.91 ∼ 7.48 × 10⁻²⁴ cm³) of xK₂O-O-(14-x)Na₂O-14Nb₂O₅-72TeO₂ glasses were estimated. We note that these values are large in comparison with the values of Rₓₐ (16.44 ∼ 17.02 cm mol⁻¹) and aₚ (6.58 ∼ 6.72 × 10⁻²⁴ cm³) for xNa₂O-O-(14-x)Nb₂O₅-72TeO₂ glasses.

The values of the relative permittivity at a frequency of 10 kHz, ε, for the various samples are shown in Figure 5 as a function of the measuring temperature. The values of ε, for the 14Na₂O-14Nb₂O₅-72TeO₂ and 10K₂O-4Na₂O-14Nb₂O₅-72TeO₂ glasses were 28 and 29, respectively. In both cases, the relative permittivity increased slightly upon increasing the temperature, but no anomalous temperature dependence was observed.

Figure 6 shows the XRD patterns for the heat-treated samples of the xK₂O-O-(14-x)Na₂O-14Nb₂O₅-72TeO₂ (x = 0 ∼ 14) glasses. The formation of a cubic crystalline phase was confirmed in the samples having x = 6, 8, and 10 mol%, but the samples showed no impurity phases. The diameter of the particles in 10K₂O-4Na₂O-14Nb₂O₅-72TeO₂, as a typical example, was estimated from the full width at half maximum (FWHM) of the X-ray diffraction peak by using Scherrer’s equation [23], L = 0.9 λ/Beos θ, where λ is the wavelength of the X-ray radiation (λ = 0.154 nm), B is the FWHM of the peak (radians) corrected for instrumental broadening, θ is the Bragg angle, and L is the particle size (nm). The average particle size of the 10K₂O-4Na₂O-14Nb₂O₅-72TeO₂ glass-ceramics was 40 nm. According to Coble’s theory [24], the activation energy of grain growth can be calculated using the Arrhenius equation

\[ \frac{d \ln k}{dT} = \frac{E}{RT^2} \]  \hspace{1cm} (3)

where k is the specific reaction rate constant, E is the activation energy, T is the absolute temperature, and R is the ideal gas constant.

Jarcho and coworkers [25] discovered that the value of k was related directly to the grain size. Thus, modification and integration of Eq. (3) provides
Table 3. Values of $T_g$ and $T_x$ for the 10K$_2$O-4Na$_2$O-15Nb$_2$O$_5$-72TeO$_2$ Glass in the Temperature Range 50$\sim$900 °C at Different Heating Rates

<table>
<thead>
<tr>
<th>Heating rate</th>
<th>$T_g$ (°C)</th>
<th>$T_x$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 °C/min</td>
<td>366.34</td>
<td>468.71</td>
</tr>
<tr>
<td>20 °C/min</td>
<td>368.61</td>
<td>476.27</td>
</tr>
<tr>
<td>25 °C/min</td>
<td>373.42</td>
<td>481.13</td>
</tr>
<tr>
<td>30 °C/min</td>
<td>377.32</td>
<td>484.28</td>
</tr>
</tbody>
</table>

Figure 7. Plot of log (grain size of a cubic crystalline phase formed in the 10K$_2$O-4Na$_2$O-14Nb$_2$O$_5$-72TeO$_2$ glass heat-treated at various temperatures) versus the reciprocal of absolute temperature ($1/T$) × 1000.

\[ \log D = \left( -\frac{E}{2.303R} \right) / T + A \]  

where \( D \) is the grain size and \( A \) is intercept. From a plot of \( \log D \) versus the reciprocal of absolute temperature \((1/T)\) from Eq. (3), we obtained the straight line shown in Figure 7. The slope of the line gives the activation energy of grain growth of a cubic crystalline phase in the 10K$_2$O-4Na$_2$O-14Nb$_2$O$_5$-72TeO$_2$ glass. The activation energy of grain growth of a cubic crystalline phase was determined to be 7.92 kJ/mol. The thermal behavior of the 10K$_2$O-4Na$_2$O-14Nb$_2$O$_5$-72TeO$_2$ glass was investigated through DTA. The values of $T_g$ and $T_x$ for the 10K$_2$O-4Na$_2$O-14Nb$_2$O$_5$-72TeO$_2$ glass in the temperature range 50$\sim$900 °C with different heating rates (10, 20, 25, and 30 °C/min) are given in Table 3.

The energy of crystallization of a cubic crystalline phase in 10K$_2$O-4Na$_2$O-14Nb$_2$O$_5$-72TeO$_2$ glass was calculated from the $T_x$ values in Table 3 using Kissinger’s or Redhead’s equation, as follows [26]:

\[ \ln (\Phi / T_p^2) = -\frac{E}{RT_p} + \text{const.} \]  

where \( \Phi \) is the heating rate, \( T_p \) is the peak temperature, and \( R \) is the ideal gas constant. As shown in Figure 8, the plot of $\ln (\Phi / T_p^2)$ vs. \((1000/T_p)\) for the PC sample was a straight line. The energy required for the phase transformation from the 10K$_2$O-4Na$_2$O-14Nb$_2$O$_5$-72TeO$_2$ glass to a cubic crystalline phase was calculated from the slope of the straight line to be 190.74 kJ/mol.

As demonstrated by many authors, TeO$_2$-based glasses have various unique, excellent optical properties relative to the other oxide glasses, such as silicate, borate, and phosphate. One of the points to be overcome in TeO$_2$-based glasses for optical applications is the refractive index and relative permittivity. In one such attempt, Yoko and coworkers measured the third-order nonlinear optical susceptibilities, $\chi^{(3)}$, of various TeO$_2$-based glasses having high refractive indexes, they reported that TeO$_2$-based glasses display very large values of $\chi^{(3)}$. In the present study, all of the values of refractive index, relative permittivity, and density of K$_2$O-Na$_2$O-Nb$_2$O$_5$-TeO$_2$ glasses were larger than those of Na$_2$O-Nb$_2$O$_5$-TeO$_2$ glasses. Thus, the measurement of $\chi^{(3)}$ for K$_2$O-Na$_2$O-Nb$_2$O$_5$-TeO$_2$ glasses might provide interesting results.

Conclusions

In summary, the thermal stabilities and physical and optical properties of xK$_2$O-(14-x)Na$_2$O-14-Nb$_2$O$_5$-72TeO$_2$ (x = 0$\sim$12 mol%) glasses, some of whose glass-ceramics show second harmonic generation, have been identified and studied. The glasses consisting of ca. 10 mol% K$_2$O show high thermal stabilities with values of $\Delta T = T_x-T_g$ of ca. 105 °C against crystallization, where $T_g$ and $T_x$ are the glass transition and crystallization on-
set temperatures, respectively. The values of the refractive indices, relative permittivities, and densities of the K$_2$O-Na$_2$O-Nb$_2$O$_5$-TeO$_2$ glasses were all larger than those of the Na$_2$O-Nb$_2$O$_5$-TeO$_2$ glasses. The activation energy of grain growth of the cubic crystalline phase in the 10K$_2$O-4Na$_2$O-14Nb$_2$O$_5$-72TeO$_2$ glass was 7.92 kJ/mol. The energy required for the phase transformation from the 10K$_2$O-4Na$_2$O-14Nb$_2$O$_5$-72TeO$_2$ glass to cubic crystalline phase was 190.74 kJ/mol. We believe that a study of the optical and physical properties of TeO$_2$-based glasses would have a large impact on the field of solid laser and nonlinear optical materials.

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**References**