Temperature Dependence of Vickers Hardness for TeO₂-Based and Soda-Lime Silicate Glasses

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テルライト系及びソーダ石灰ケイ酸塩ガラスのビッカース硬度の温度依存性

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The temperature dependence of Vickers hardness (H) of TeO₂-based glasses such as 15Na₂O·15ZnO·70TeO₂ as host glasses for rare-earth doped optical amplifier was measured from room temperature to the glass transition region. The following features were found; (1) crack formation under the indenter easily occurs, the Vickers hardness at room temperature being around 3 GPa; (2) the temperature coefficient of the hardness, dH/dT , is around -4.5×10^{-3} GPa·K⁻¹; (3) the relative change of hardness with temperature is closely related to thermal expansion coefficient, and hardness sharply decreases in the glass transition region. It was demonstrated that TeO₂-based glasses are fragile even from the point of view of mechanical properties. The reason for poor mechanical performance in TeO₂-based glasses is their weak bond strength and open atomic packing structures. The hardness ($H=4.8$ GPa) of a transparent glass-ceramic (with nanocrystalline particles) of 15K₂O·15Nb₂O₅·70TeO₂ showing second harmonic generation is much larger than that of the precursor glass ($H=3.3$ GPa), meaning that the improvement in the fragile character of TeO₂-based glasses is due to crystallization. A soda-lime silicate glass of 14Na₂O·13CaO·73SiO₂ has a value $dH/dT = -6.5 \times 10^{-3}$ GPa·K⁻¹, and in contrast to TeO₂-based glasses, its hardness decrease in the glass transition region is gradual, and a value $H \approx 2$ GPa is obtained even at the glass transition temperature.

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1. Introduction

Tellurium oxide (TeO₂)-based glasses are of scientific and technical interest on account of their various unique properties, and have been considered as promising materials for use in optical amplifier because of their low phonon energy or in nonlinear optical devices because of their large third-order nonlinear susceptibility.^{1,2)} Recently, optically transparent TeO₂-based glass-ceramics showing second harmonic generation have been discovered.^{3,4)} The structure of TeO₂-based glasses is also of interest, because there are two types of the basic structural units, i.e., TeO₄ trigonal bipyramid (tbp) and TeO₃ trigonal pyramid (tp). In order to develop TeO₂-based glasses and glass-ceramics as new optical functional materials, an understanding of mechanical properties is necessary, because generally poor mechanical properties of glasses and ceramics limit their use in many applications. To our best knowledge, however, the study of mechanical properties such as hardness and fracture toughness in TeO₂-based glasses is scarce.

In this paper, we focus our attention on the temperature dependence of Vickers hardness of TeO₂-based glasses. Hardness, which is a measure of the resistance to deformation, is one of the important mechanical properties. It should be pointed out that even in SiO₂-based glasses the study of the temperature dependence of hardness has been limited to a few papers,^{5,6)} although many studies of hardness of various silicate and borate glasses at room temperature have been carried out. Therefore, we also measured the temperature dependence of Vickers hardness of a soda-lime silicate glass for comparison with the behavior of TeO₂-based glasses. From the temperature dependence of viscosity and heat capacity changes in the glass transition region, it has been recognized that TeO₂-based glasses belong to the category of "fragile" glass-forming liquids in the strong/fragile classification proposed by Angell.⁷⁻⁹⁾ It is of interest to examine mechanical proper-

ties of TeO₂-based glasses from the point of fragility concept.

2. Experimental procedure

2.1 Glass preparation

In this study, TeO₂-based glasses of 10K₂O·20WO₃·70TeO₂ (designated as KWTe glass), 15Na₂O·15ZnO·70TeO₂ (NaZTe glass), 15K₂O·15Nb₂O₅·70TeO₂ (KNbTe glass) were examined. These glasses have the following features: The KWTe glass is thermally stable against crystallization and the formation of W–O–Te network structure has been proposed,¹⁰⁾ the NaZTe glass is thermally very stable and has been considered as a host glass for rare earth-doped optical amplifier glass fiber.¹⁾ The KNbTe glass is converted into transparent glass-ceramics showing second harmonic generation through careful heat treatments.^{3,4)} A soda-lime silicate glass with a composition of 14Na₂O·13CaO·73SiO₂ commercially available is used.

The TeO₂-based glasses were prepared using a conventional melt-quenching method. Commercial powders of reagent grade Na₂CO₃, K₂CO₃, ZnO, WO₃, Nb₂O₅ and TeO₂ were mixed and melted in a platinum crucible at about 800–1000°C for 30 min in an electric furnace. After melting, the melt was poured onto iron plate and pressed to a thickness of about 2 mm using another iron plate heated at about 250–300°C. The glasses were annealed at a temperature of $T_g + 10^\circ\text{C}$ to eliminate internal stress in the glasses. A transparent glass-ceramic with the composition of 15K₂O·15Nb₂O₅·70TeO₂ was prepared through the two step heat treatment of 375°C, 5 h + 425°C, 5 h.

2.2 Vickers hardness measurements and analyses

The temperature dependence of Vickers hardness of the glasses was measured using a high-temperature type hardness equipment of Nikon QM-2 in the temperature range from room temperature to around T_g in a vacuum of $1.33 \times$

10^{-3} Pa. The applied load was 490 mN and the loading time was 15 s. The temperature of the diamond pyramid indenter was kept to that of the samples within $\pm 1^\circ\text{C}$. Vickers hardness at room temperature was also measured using Akashi MVK-100 in air. The applied loads were 245, 490, 980 mN, and the time of loading is 15 s.

In a Vickers indenter test under an applied load of P , a deformation-fracture pattern as drawn schematically in Fig. 1 is observed, where a and C are characteristic indentation diagonal and crack lengths. One can evaluate Vickers hardness H using Eq. (1):

$$H = P / \alpha_0 a^2 \quad (1)$$

where α_0 is an indenter constant of 2.15 in the present experiment-used diamond pyramid indenter. Fracture toughness K_C , which is a measure of the resistance to fracture, is expressed by the following Eq. (2):

$$K_C = P / \beta_0 C^{3/2} \quad (2)$$

where β_0 is a function of Young's modulus E and hardness H , and many models for the estimation of β_0 have been proposed are summarized by Ponton and Rawlings.¹¹⁾ For example, Anstis et al.¹²⁾ proposed the following equation:

$$K_C = 0.016 (E/H)^{1/2} (P/C^{3/2}) \quad (3)$$

The above Eq. (3) is almost the same as the following equation recommended by Japanese Industrial Standards (JIS) for ceramics,¹³⁾

$$K_C = 0.018 (E/H)^{1/2} (P/C^{3/2}) \quad (4)$$

Equation (4) gives fairly good estimate of the fracture toughness of glasses exhibiting normal indentation process.¹⁴⁾ In the inclusion core model proposed by Tanaka,¹⁵⁾ the Vickers indentation fracture toughness is expressed by the following equation

$$K_C = 0.035 (E/H)^{1/4} (P/C^{3/2}) \quad (5)$$

The C/a ratio is also an important parameter for the evaluation of brittleness of materials proposed by Lawn and Marshall¹⁶⁾ and Sehgal et al.,¹⁴⁾ because it is related to the ratio of hardness and the fracture toughness, i.e., H/K_C ratio. The relation between C/a and H/K_C is expressed by the following equations:^{14),16)}

$$C/a = \Psi (H/K_C)^{2/3} P^{1/6} \quad (6)$$

$$\Psi = A E^{1/3} / H^{1/2} \quad (7)$$

where A is a constant. For normal glasses such as soda-lime silicate glasses the parameter Ψ has a value of 0.0054–0.0058.¹⁴⁾ Sehgal et al.¹⁴⁾ have proposed that the C/a ratio should be measured for the evaluation of brittleness of glass

through Vickers indentation test.

3. Results and discussion

3.1 Vickers hardness at room temperature

The values of a and C for the KWTe glass at room temperature in air are shown in Fig. 2 as a function of applied load, where the data for some silicate glasses reported by Sehgal et al.¹⁴⁾ are included. Since the shapes of impressions and cracks in Vickers indenter tests for the KWTe glass were the same as Fig. 1 and the slopes of a and C against load P in Fig. 2 are 0.51 and 0.67, respectively, Eqs. (1) and (2) can be applied for the results shown in Fig. 2. It is seen that the value of a of the KWTe glass is slightly higher than that of silicate glasses. However, a large difference in the C value is observed in comparison with the KWTe glass and silicate glasses. The C/a values obtained for the KWTe glass are plotted against load in Fig. 3. The C/a values of the KWTe glass are larger than those of silicate glasses because of the large difference in the C value shown Fig. 2. These results clearly demonstrate that the crack formation in the KWTe glass occurs easily compared with the case in silicate glasses. The slope of C/a against load P in Fig. 3 is 0.21, meaning that Eq. (6) is well hold for the KWTe glass as similar to silicate glasses.

The values of Vickers hardness H obtained in the present study for the TeO_2 -based glasses at room temperature in a vacuum of 1.33×10^{-3} Pa are given in Table 1. That is, 2.5 GPa for the KWTe glass, 2.6 GPa for the NaZTe glass and 3.3 GPa for the KNbTe glass. Sidkey et al.¹⁷⁾ reported the value of microhardness of about 1.5 GPa for V_2O_5 - TeO_2 glasses. The value of $H=6.0$ GPa is obtained for the soda-lime silicate glass. It is clear that the hardness of TeO_2 -based glasses is relatively about the half of those for soda-lime silicate glasses,^{14),18),19)} meaning that the deformation due to applied load in TeO_2 -based glasses occurs easily compared with silicate glasses.

Fig. 1. Typical deformation-fracture pattern showing median crack in Vickers indentation test.

Fig. 2. Values of a and C in median cracks obtained in Vickers indentation test with various loads in air. $\circ$ $10\text{K}_2\text{O} \cdot 20\text{WO}_3 \cdot 70\text{TeO}_2$ glass, $\bullet$ soda-lime silicate glass,¹⁴⁾ $\square$ alkaline earth silicate glass.¹⁴⁾

Fig. 3. Values of C/a in median cracks obtained in Vickers indentation test with various loads in air. $\circ$ $10\text{K}_2\text{O}\cdot 20\text{WO}_3\cdot 70\text{TeO}_2$ glass, $\bullet$ soda-lime silicate glass,¹⁴⁾ $\square$ alkaline earth silicate glass.¹⁴⁾

Glass undergoes both compression and shear during the process of deformation in indentation test, and consequently the observed deformation comprises elastic deformation, plastic flow and densification.^{20)–24)} It is recognized that so-called normal glasses such as soda-lime silicate glasses deform largely by a shear-dominated flow process, which is necessary to reconstruct the bond configuration, i.e., bonds must be continuously broken and re-engaged with new neighbors. On the other hand, so-called anomalous glasses such as fused SiO_2 glass deform by a pressure-dominated densification process. It is expected that TeO_2 -based glasses belong to the category of normal glasses, because they show high thermal expansion coefficients, negative temperature coefficient and positive pressure coefficient of bulk modulus.⁵⁾ TeO_2 -based glasses are known to show weak bonding features such as low melting point, low glass transition temperature and low phonon energy, although the network structure is three-dimensional. It is, therefore, considered that in TeO_2 -based glasses a weak bond strength would result in a high percentage of bond breaking and irreversible plastic flow during indentation, leading to small hardness.

It is known that there are two strategies to design glasses with high mechanical properties such as high bulk modulus.²⁵⁾ One is to select compositions which lead to enhance bond strength between atoms, and the other is to

increase packing density of constituent atoms. It has been reported that bulk moduli in various silicate and borate glasses decrease linearly with increasing mean atomic volume (i.e., packing density).²⁵⁾ The mean atomic volume in TeO_2 -based and soda-lime silicate glasses, which were calculated from their densities, are given in Table 1. It is seen that TeO_2 -based glasses have the values of $9.5\text{--}9.8 \times 10^{-6} \text{ m}^3 \text{ g-atom}^{-1}$, which are much larger than that ($8.3 \times 10^{-6} \text{ m}^3 \text{ g-atom}^{-1}$) in soda-lime silicate glass. The large mean atomic volumes in TeO_2 -based glasses indicate that they have open atom packing structures. This would be also one reason for small Vickers hardnesses in TeO_2 -based glasses.

3.2 Temperature dependence of Vickers hardness

The temperature dependence of Vickers hardness of the TeO_2 -based glasses in a vacuum is shown in Figs. 4 and 5. For example, in the case of the KWTe glass, the hardness in the temperature range of room temperature to 300°C decreases almost linearly with increasing temperature, but above 300°C it drops sharply. At the glass transition temperature $T_g = 344^\circ\text{C}$, the hardness is almost zero in the GPa scale. The temperature coefficient of the hardness below 300°C is $dH/dT = -4.6 \times 10^{-3} \text{ GPa} \cdot \text{K}^{-1}$, which was determined from a least square fitting of the data. Similar temperature dependencies are observed in other TeO_2 -based glasses and also in a soda-lime silicate glass, and the values of dH/dT are given in Table 1. It is seen that the TeO_2 -based glasses have small temperature coefficients of hardness compared with that of a soda-lime silicate glass.

Elastic properties are among physical properties which depend on the forces between atoms in solids. As the temperature increases, thermal expansion increases the separation between atoms and slightly decreases the forces between atoms, leading to the decrease in elastic modulus with increasing temperature. It is obvious that the decrease in bond strength causes the decreases in hardness. In other words, the data shown in Figs. 4 and 5 suggest that the bond strength in TeO_2 -based glasses decreases in an order of $4\text{--}5 \times 10^{-3} \text{ GPa} \cdot \text{K}^{-1}$ with increasing temperature.

As seen in Table 1, the thermal expansion coefficient, α , of a soda-lime silicate glass is smaller than those of the TeO_2 -based glasses. But, the temperature coefficient of hardness of a soda-lime silicate glass is larger than those of TeO_2 -based glasses. We estimated the relative change in hardness, i.e., $1 - \Delta H/H_{\text{RT}}$, where H_{RT} is the hardness at room temperature and ΔH is the difference between hardness H at a given temperature and H_{RT} . The estimated values are given in Table 1. It is seen that the temperature coefficients of the relative change in hardness of the TeO_2 -

Table 1. Some Properties of TeO_2 -Based and Soda-Lime Silicate Glasses Examined in This Study. T_g : Glass Transition Temperature, ρ : Density, α : Thermal Expansion Coefficient ($50\text{--}200^\circ\text{C}$), H : Vickers Hardness, dH/dT : Temperature Coefficient of Hardness below T_g , $d(1 - \Delta H/H_{\text{RT}})/dT$: Temperature Coefficient of Relative Change in Hardness ($\Delta H = H_{\text{RT}} - H$, H_{RT} is the Hardness at Room Temperature) $\bar{V}_m$ is the Mean Atomic Volume

Sample	T_g ($^\circ\text{C}$)	ρ ($\times 10^3 \text{ kg m}^{-3}$)	α (K^{-1})	H (GPa)	dH/dT (GPa K^{-1})	$d(1 - \Delta H/H_{\text{RT}})/dT$ (K^{-1})	$\bar{V}_m$ ($\text{m}^3 \text{ g-atom}^{-1}$)
KWTe	344	5.50	188×10^{-7}	2.5	-4.6×10^{-3}	-1.8×10^{-3}	9.52×10^{-6}
NaZTe	264	4.94	225×10^{-7}	2.6	-4.5×10^{-3}	-1.7×10^{-3}	9.46×10^{-6}
KNbTe (Glass)	375	4.46	156×10^{-7}	3.3	-5.0×10^{-3}	-1.5×10^{-3}	9.82×10^{-6}
KNbTe (Crystallized)	---	5.01	124×10^{-7}	4.8	-6.3×10^{-3}	-1.3×10^{-3}	9.19×10^{-6}
Soda-lime	555	2.50	85×10^{-7}	6.0	-6.6×10^{-3}	-1.1×10^{-3}	8.27×10^{-6}

Fig. 4. Temperature dependence of hardness obtained in a vacuum of 1.33×10^{-3} Pa.

○ 10K₂O·20WO₃·70TeO₂ glass, ● soda-lime silicate glass.

Fig. 5. Temperature dependence of hardness obtained in a vacuum of 1.33×10^{-3} Pa.

○ 15Na₂O·15ZnO·70TeO₂ glass, ● 15K₂O·15Nb₂O₅·70TeO₂ glass, □ 15K₂O·15Nb₂O₅·70TeO₂ glass-ceramic.

based glasses are much larger than that of a soda-lime silicate glass and are closely related to the thermal expansion coefficient, i.e., the samples with larger α tend to have larger relative change in hardness.

The temperature dependencies of a , C and C/a ratio of the KWTe glass are shown in Figs. 6 and 7. It should be pointed out that the crack formation in the indentation test with $P=490$ mN was observed at the temperatures below 320 °C, but no crack was observed at the temperatures above 320 °C. It is seen that the value of a increases gradually with increasing temperature. On the other hand, the value of C increases gradually up to 250 °C, but decreases at further high temperatures. It is considered that at temperatures below 250 °C the weakening of the bond strength due to thermal expansion would affect mainly on the deformation (i.e., the value of a) and crack propagation (i.e., the value of C). In the temperature region of 250–300 °C, the hardness decreased linearly, but the crack propagation was depressed. It is considered that some plastic deformation which does not affect hardness value occurs easily at this temperature region and thus the radius of curvature at crack tip becomes largely. Glass becomes fluid at around T_g (above 300 °C), meaning that plastic deformation (atomic displacement and/or atomic rearrangement) can absorb applied stress energy through atomic rear-

Fig. 6. Temperature dependence of a and C in median cracks obtained in Vickers indentation test with a load of 490 mN in a vacuum of 1.33×10^{-3} Pa. The sample is 10K₂O·20WO₃·70TeO₂ glass.

Fig. 7. Temperature dependence of C/a in median cracks obtained in Vickers indentation test with a load of 490 mN in a vacuum of 1.33×10^{-3} Pa. The sample is 10K₂O·20WO₃·70TeO₂ glass.

rangements. Such a large plastic deformation would suppress the occurrence of catastrophic crack propagation. This would be the reason that the value of C decreases at around T_g and no crack formation occurs above 320 °C.

As seen in Figs. 4 and 5, the hardness of the TeO₂-based glasses decreases sharply at the glass transition, but in the soda-lime silicate glass the change in the hardness is gradual. Fragility concept has been introduced to characterize the structural relaxation behavior of glass in the glass transition region, and the degree of fragility has been evaluated quantitatively from the temperature dependence of viscosity and the change in heat capacity at the glass transition. It has been recognized that TeO₂-based glasses are "fragile" not only from viscosity change but also from heat capacity change. That is, in TeO₂-based glasses, Te–O–Te bonds in the network structure are weak and bond breakings occur easily in the glass transition region, leading to the steep temperature dependence of viscous flow and to large configurational entropy changes.^{7)–10)} As reported by Lee et al.,⁷⁾ sodium silicate glasses are more strong compared with Li₂O–TeO₂ glasses in the fragility concept. That is, the change in viscosity and heat capacity at around T_g in alkali silicate glasses are more gradual and smaller than those in alkali tellurite glasses. The behavior of the temperature dependence of the hardness of the TeO₂-

based and soda-lime silicate glasses in the glass transition region shown in Figs. 4 and 5 is similar to that of the temperature dependence of viscosity. Since the rapid decrease in viscosity causes the rapid increase in deformation under applied stress, the presence of a close correlation between the temperature dependence of hardness and viscosity would be reasonable.

The present study has clarified that TeO₂-based glasses have the following features: the crack formation under an indentation test occurs easily, the Vickers hardness at room temperature is around 3 GPa, the relative change in the hardness with temperature is larger than that of a soda-lime silicate glass, and the hardness decreases steeply in the glass transition region. These features demonstrate that TeO₂-based glasses are fragile even from the point of mechanical properties. That is, TeO₂-based glasses are mechanically "fragile."

Here, we try to estimate the value of fracture toughness of TeO₂-based glasses. The Young's modulus E and Vickers hardness H of, for example, soda-lime silicate glasses are $E \approx 70$ GPa and $H \approx 5.5$ GPa.¹⁴⁾ On the other hand, TeO₂-based glasses have $E \approx 30\text{--}40$ GPa^{17),26)} and $H \approx 3.3$ GPa (obtained in the present study). These data indicate that the value of Ψ (Eq. (7)) in TeO₂-based glasses is almost the same as that in soda-lime silicate glasses, i.e., $\Psi(\text{soda-lime})/\Psi(\text{TeO}_2) = 0.95$. Therefore, the results on C/a shown in Fig. 3 suggest that the fracture toughness K_C of TeO₂-based glasses is small compared with silicate glasses. From Eq. (4), the value of $K_C \approx 0.23 \text{ MPa} \cdot \text{m}^{1/2}$ was estimated by using the value of $E = 40$ GPa. Similarly, the value of $K_C \approx 0.23 \text{ MPa} \cdot \text{m}^{1/2}$ was obtained by using Eq. (5). These results suggest that the fracture toughness in TeO₂-based glasses is extremely small and is almost one third compared with those of silicate glasses.¹⁸⁾ The measurement of K_C in TeO₂-based glasses is now under consideration.

3.3 Vickers hardness of transparent TeO₂-based glass-ceramic

The temperature dependencies of the hardness of the KNbTe glass and a transparent glass-ceramic showing second harmonic generation are shown in Fig. 5. It should be pointed out that the decrease in the hardness of the KNbTe glass in the glass transition region is gradual compared with those of the KWTe and NaZTe glasses. This difference would be due to the difference in the thermal stability against crystallization. That is, the KWTe and NaZTe glasses have the high thermal stability, leading to no crystallization peak in DTA patterns (heating rate: $10 \text{ K} \cdot \text{min}^{-1}$). But, the KNbTe glass is easily crystallized in the glass transition region, leading to a transparent crystallized sample. It is, therefore, considered that in the KNbTe glass some amounts of crystal nucleation might be occurred during the indentation test in the glass transition region.

The glass-ceramic has a value of $H = 4.8$ GPa at room temperature, which is much larger than that ($H = 3.3$ GPa) of precursor glass, and has a value of $dH/dT = -6.3 \times 10^{-3} \text{ GPa} \cdot \text{K}^{-1}$, which is very close to that of the soda-lime silicate glass. The temperature dependence of the relative change in the hardness for the transparent glass-ceramic is given in Table 1. It is seen that the glass-ceramic has a small temperature coefficient compared with the precursor glass. The thermal expansion coefficient of the glass-ceramic is smaller than that of the precursor glass, indicating again that the thermal expansion coefficient is one of the important factor for the temperature dependence of the relative change in hardness.

The results shown in Fig. 5 demonstrate that the hardness of TeO₂-based glasses are largely improved due to crystallization. In the transparent glass-ceramic of $15\text{K}_2\text{O} \cdot$

$15\text{Nb}_2\text{O}_5 \cdot 70\text{TeO}_2$, the presence of the glassy phase is not detected in the X-ray diffraction analyses and the crystallization behavior is bulk crystallization,²⁷⁾ and the mean atomic volume ($9.19 \times 10^{-6} \text{ m}^3 \cdot \text{g-atom}^{-1}$) is much smaller than that in the glassy sample. These indicate that an excess free volume in the transparent glass-ceramic would be extremely small. From the values of thermal expansion coefficient (see Table 1), it is considered that the bond strength in the crystalline phase would be stronger than that in the glassy state. It is, therefore, expected a large improvement in mechanical properties of TeO₂-based glasses due to crystallization. It has been reported that the bulk moduli of $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ and $\text{Li}_2\text{O} \cdot 4\text{SiO}_2$ glasses are largely increased due to crystallization, although the crystallization causes only small increase in density (i.e., small decrease in mean atomic volume).²⁵⁾ Thus, it is expected that KNbTe glass-ceramics also have larger bulk modulus compared with KNbTe glass due to crystallization.

Recently, besides the observation of the second harmonic generation in transparent glass-ceramics, the present authors' group succeeded in preparing transparent TeO₂-based glass-ceramics doped by Er^{3+} and found that the intensity of frequency upconversion fluorescence at around 550 nm due to the $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ transition in the glass-ceramics is strong compared with that in their precursor glass.²⁸⁾ Therefore, the large improvement in the hardness of TeO₂-based glasses due to the glass-ceramic processing is very important for technical applications of TeO₂-based materials with excellent optical properties. The transparent glass-ceramic of $15\text{K}_2\text{O} \cdot 15\text{Nb}_2\text{O}_5 \cdot 70\text{TeO}_2$ consists of small crystallites with the average particle size of 10–20 nm,²⁷⁾ and it is of interest to examine other mechanical properties such as Young's modulus and fracture toughness in ceramics consisting of nanocrystallites.

4. Conclusions

As described in the introduction, information on mechanical properties of TeO₂-based glasses is scarce compared to the study of structure and optical properties. In this study, the temperature dependence of Vickers hardness H from room temperature to the glass transition region of some TeO₂-based glasses was measured for the first time. The temperature dependence of a soda-lime silicate glass was also measured for comparison. TeO₂-based glasses have the hardness of around 3 GPa at room temperature and are very brittle. It was found that the hardness of TeO₂-based glasses drops sharply in the glass transition region. A transparent glass-ceramic of $15\text{K}_2\text{O} \cdot 15\text{Nb}_2\text{O}_5 \cdot 70\text{TeO}_2$ has a high hardness ($H = 4.8$ GPa) comparable to soda-lime silicate glasses. It was demonstrated that TeO₂-based glasses, which were examined in the present study, are "fragile" even from the point of mechanical properties. Recently, Sehgal and Ito²⁹⁾ reported that a higher molar volume is a key factor for reducing the brittleness of soda-lime silicate glasses. It is of interest to examine the correlation between molar volume and hardness of various TeO₂-based glasses, and such information might give an important clue for improvement in mechanical properties.

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