Research Article

Nanocrystallization of Vanadium Borophosphate Glass for Improving the Electrical and Catalytic Properties

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Received 20 March 2015; Accepted 13 May 2015

Academic Editor: Min Liu

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$75\text{V}_2\text{O}_5\text{-}10\text{P}_2\text{O}_5\text{-}15\text{B}_2\text{O}_3$ ternary-system glasses were prepared and nanocrystallized to examine the catalytic effect and the variations in their structural and electrical properties. These glasses were annealed in a graphite mold above the glass transition temperature for 2 h and heat-treated at the crystallization temperature for 1, 3, and 5 h. Fourier transform infrared spectroscopy (FTIR) was used to analyze the structural changes in the B-O bonds after nanocrystallization, while X-ray photoelectron spectroscopy (XPS) analysis showed a decrease in V^{5+} and an increase in V^{4+} . X-ray diffraction (XRD) analysis of the structure array ($\text{BO}_3 + \text{V}_2\text{O}_5 \leftrightarrow \text{BO}_4 + 2\text{VO}_2$) verified these inferred changes. Structural changes induced by the heat treatment were confirmed by analyzing the molecular volume determined from the sample density. Conductivity and catalytic effects were discussed based on the migration of vanadate ions with different valence states due to the increase in VO_2 nanocrystallinity at 275°C . Both conductance and the catalytic effect were higher after nanocrystallization at 275°C for 1 h compared to the annealed sample. Furthermore, compared to the sample heat-treated for 1 h, the conductance and catalytic effect were increased and decreased, respectively, for samples nanocrystallized at 275°C for 3 and 5 h.

1. Introduction

Vanadate glasses containing large amounts of V_2O_5 have multivalent ions of various states mixed in their structure. These glasses have been developed for infrared transmission and as atomic-exchange electroconductive glasses using electron conduction. Studies focusing on improving the performance of these glasses involve changing the electrical conduction properties through low valency (V^{4+}) to high valency (V^{5+}) metal-ion electron hopping [1], changing the catalytic properties for the oxidation reaction by altering the valency change between V^{4+} and V^{5+} [2], and examining the correlation between the glass composition and its characteristics while focusing on the type and condition of V ions or the type and the amount of alkali or alkaline earth metals [3–7].

In 2012, we substituted B_2O_3 for P_2O_5 to improve the chemical resistance and electrical conductivity of vanadium phosphate-based glasses, and we were able to investigate the significance of the correlation between the resulting structure and the electrical, thermal, and chemical properties

[6]. However, the effect of the substitution was insignificant. Moreover, the analysis of the catalytic activity of the oxidation reaction, which is characteristic of V_2O_5 , with respect to the vanadate glass was insufficient. On the other hand, if vanadate glass is crystallized and the structure becomes denser, electron tunneling in the glass would occur with a higher frequency [8]. This behavior leads to frequent valency changes in the V cation. It is hypothesized that this change influences the change in the catalytic effect and electrical conductivity. In particular, if the nanocrystalline phases are generated, the specific surface area of the crystalline phases will be maximized. So, property changes due to crystallization appear to be more prominent.

In this study, P_2O_5 was used as a glass former, to which V_2O_5 or other metal oxides are added in order to achieve V_2O_5 -like characteristics. We maximized the electrical conductivity and catalytic properties of $\text{V}_2\text{O}_5\text{-B}_2\text{O}_3\text{-P}_2\text{O}_5$ ternary glass by maximizing the amount of the substitute (B_2O_3 for P_2O_5) to form $75\text{V}_2\text{O}_5\text{-}15\text{B}_2\text{O}_3\text{-}10\text{P}_2\text{O}_5$ ternary glass. It was confirmed that nanocrystallizing this ternary

FIGURE 1: Differential scanning calorimetry (a) and resulting heat-treatment profile (b) for all the V_2O_5 -based glasses used in this study.

glass produces $\text{VO}_2(\text{VO}_4)$, $\text{V}_2\text{O}_5(\text{VO}_5)$, and $\text{B}_2\text{O}_3(\text{BO}_4)$ crystalline phases, and the structural change in the nanocrystalline phase was caused by increasing the duration of heat treatment for crystallization. From the results, it was evident that this behavior affected the ratio of V^{5+} to V^{4+} .

We presumed that the changes in the electrical conduction and catalytic properties were induced by the heat treatment. The causes behind the characteristic changes and the action mechanism were investigated through qualitative and quantitative analysis of X-ray diffraction (XRD) patterns, X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared (FTIR) spectroscopy. We examined the quantitative physical properties such as density and molar volume to verify the predicted action mechanism.

2. Materials and Methods

2.1. Glass Preparation and Nanocrystallization. $75\text{V}_2\text{O}_5$ - $15\text{B}_2\text{O}_3$ - $10\text{P}_2\text{O}_5$ glass samples were prepared using reagent-grade $\text{NH}_4\text{H}_2\text{PO}_4$, V_2O_5 , and B_2O_3 (Junsei Chemical Co., Ltd., Japan). The constituents were mixed in an alumina mortar for 10 min to produce multiple batches. Well-mixed batches were first melted in an alumina crucible using an electrical furnace at 200°C for 1 h (first calcination), subsequently at 500°C for 2 h (second calcination), and finally at 800°C for 2 h. The resultant melt was quenched between two stainless steel plates.

The as-prepared sample was crushed in an automatic grinding mixer and sieved through a 325 mesh. This powder (particle size below $44\ \mu\text{m}$) was used for differential scanning calorimetry (DSC), XRD, XPS, FTIR, and thermogravimetric analysis (TGA) measurements.

DSC was performed on the samples using an SDT (SDT Q600, TA instrument, USA) to determine both the glass transition (T_g) and the crystallization (T_c) temperatures, as shown in Figure 1(a). The glasses were annealed in a graphite

mold above T_g for 4 h and heat-treated at T_c for 1, 3, or 5 h. Detailed heating profiles are provided in Figure 1(b).

The glass samples used for the experiments (electrical conductivity, density, and molar volume) were rectangular parallelepipeds and their surfaces were polished using SiC paper (#220–1000).

2.2. Measurement. XRD measurements were taken in a Rigaku Co. RINT 2000 using $\text{Cu-K}\alpha$ radiation in the 10 – $80^\circ 2\theta$ range with a step size of 0.02° . The existence of the nanocrystal phase was confirmed using the resultant XRD patterns. The nanocrystal phases were observed by field emission scanning electron microscopy (FE-SEM, Carl Zeiss, Supra 25).

We investigated the structural changes using FTIR spectroscopy. Powdered samples mixed with KBr (mixing ratio 1:1200) were prepared and dried at 100°C in a desiccator to form pellets. A Spectrum GX (Perkin Elmer Co, USA) spectrometer was used to perform FTIR. Room temperature IR spectra were recorded from 400 to $1400\ \text{cm}^{-1}$ (injection number of times: 20; resolving power: $2\ \text{cm}^{-1}$).

XPS was used to analyze the change in the valency of vanadium cations in the glass. XPS measurements were taken using the ESCALAB250 XPS system and the Theta Probe XPS system using monochromatic $\text{Al-K}\alpha$ ($h\nu = 1486.6\ \text{eV}$) radiation. The analysis area was $400\ \mu\text{m}$ and the data was compensated using C1s ($284.6\ \text{eV}$) as the reference.

The catalytic properties and electrical conductivity are the main characteristics considered in this study. First, in order to measure the electrical conductivity of each specimen, the carrier density was measured at room temperature using a Hall-effect measurement system (HMS-3000 Hall Measurement System, ECOPIA). Furthermore, to examine the catalytic effect of the glass samples applied to the oxidation of fatty acids (linoleic acid and stearic acid) and carbon, we performed TGA on two samples obtained by mixing 20 mg of

FIGURE 2: XRD patterns of 75V₂O₅-15B₂O₃-10P₂O₅ glasses heat-treated at 275°C.

fatty acid with 20 mg of glass powder and gas chromatography with a mass spectrometer (GC-MSD) on a sample obtained by mixing 2 mg of carbon with 8 mg of glass powder. TGA measurements were obtained between room temperature and 600°C at a heating rate of 10°C/min in an atmosphere of 5 vol% using a simultaneous TGA/DSC (Q600, TA Instruments, Inc.). The fatty acids used in the experiments are reagent-grade stearic acid (95%) and technical grade linoleic acid (60–74%, GC), both from Sigma-Aldrich Co. GC-MSD measurements were obtained between room temperature and 450°C at a heating rate of 10°C·min⁻¹ in an atmosphere of He and O₂ using a 5975MSD-6890N GC (Agilent). He gas was used at a flow rate of 20 mL/min and O₂ gas was used at a flow rate of 2 mL/min.

Changes in quantitative properties due to structural changes were confirmed using the molar volume and density measurements. The densities of the glass samples were measured using the Archimedes method using a GH-200 (AND Co, Korea), and the molar volume (V_M) was calculated from the measured density using $V_M \equiv \bar{M}/\rho$ [9], where $\bar{M}$ is the average molar weight of glass.

3. Results and Discussion

3.1. Analysis of Nanocrystal Phases. Figure 2 shows the diffraction patterns of all the samples studied, which were annealed for 4 h and heat-treated at 275°C for different durations (1, 3, and 5 h). A V₂O₅ phase (V⁵⁺/JCPDS-PDF 85-0601) coexisting with the VO₂ (V⁴⁺/JCPDS-PDF 73-0514) and B₂O₃ (BO₄/JCPDS-PDF 760781) phases was detected in samples heat-treated at 275°C. As the holding time at 275°C increased, the relative amounts of VO₂ and B₂O₃ increased while the relative amount of V₂O₅ decreased; that is, VO₂

and BO₄ structures are strengthened by nanocrystallizing the 75V₂O₅-15B₂O₃-10P₂O₅ ternary glass. Combining this fact with the results of the FTIR analysis (Section 3.3), which explains the structural change of BO₃ to BO₄, the nanocrystallization of the VO₂ phase occurred and this nanocrystal was strengthened while the V₂O₅ phase was comparatively weakened as the heat treatment at 275°C progressed. This suggested that a structural change, indicated by the reaction $\text{BO}_3 + \text{VO}_5(\text{V}_2\text{O}_5) \rightarrow \text{BO}_4 + \text{VO}_4(\text{VO}_2)$, was induced by the heat treatment at 275°C. This structural change is a factor that affects the electrical conduction and catalytic properties of the vanadate glass.

Figure 3 shows the SEM images of all samples studied, which were annealed for 4 h and heat-treated at 275°C for different durations (1, 3, and 5 h). Nanocrystallines of VO₂ phase were detected in samples heat-treated at 275°C. As the holding time at 275°C increased, the amounts of nanocrystalline increased.

3.2. XPS Spectroscopy. To quantitatively determine the change in the vanadium ion valency, we performed an XPS analysis on each glass sample. The V 2p spin orbit doublet spectra of 75V₂O₅-15B₂O₃-10P₂O₅ glasses are shown in Figure 4. The XPS analysis was performed while maintaining the same X-ray energy, X-ray-to-sample positioning, and sampling time for all the four samples in accordance with the nanocrystallization conditions. V 2p peaks appeared asymmetrically in each sample, indicating that the vanadium ions are present in more than one oxidation state [10]. According to previous studies on vanadium phosphate glasses, core level spectra of V⁵⁺ appear at a binding energy (BE) of 517.3 eV, while that of V⁴⁺ appears at 516.0 eV [11–14]. Therefore, when the V 2p_{3/2} core level spectrum is fitted to the BE

FIGURE 3: SEM images of $75\text{V}_2\text{O}_5$ - $15\text{B}_2\text{O}_3$ - $10\text{P}_2\text{O}_5$ glasses (a) annealed at 225°C and heated for crystallization at 275°C for (b) 1, (c) 3, and (d) 5 h.

FIGURE 4: Core level V 2p spectra for the $75\text{V}_2\text{O}_5$ - $15\text{B}_2\text{O}_3$ - $10\text{P}_2\text{O}_5$ glasses heat-treated at 275°C .

of 517.3 eV of the V^{5+} ions and 516.1 eV of the V^{4+} ions, quantitative analysis for the concentration of V^{5+} and V^{4+} became possible [15]. The V^{5+} and V^{4+} peaks of the $75\text{V}_2\text{O}_5$ - $15\text{B}_2\text{O}_3$ - $10\text{P}_2\text{O}_5$ glass, obtained from the vanadium Gaussian-Lorentzian peaks, fitted using the least squares method, are shown in Figure 5. The relative content ratios of $\text{V}^{5+}/\text{V}_{\text{total}}$ and $\text{V}^{4+}/\text{V}_{\text{total}}$ obtained using this fit are shown in Table 1.

It was found that the content of the V^{5+} in glass was reduced and V^{4+} was increased by nanocrystallizing $75\text{V}_2\text{O}_5$ - $15\text{B}_2\text{O}_3$ - $10\text{P}_2\text{O}_5$ glass and increasing the heat treatment time for crystallization. This means that the V^{5+} to V^{4+} reduction reaction occurs during nanocrystallization at 275°C and increments in the heat treatment duration. This behavior is in agreement with the trends in the catalytic properties (Section 3.5) and electrical conductivity (Section 3.4). We have confirmed that the changes in concentration and state of vanadium ions due to nanocrystallization contribute directly to the characteristic change in the $75\text{V}_2\text{O}_5$ - $15\text{B}_2\text{O}_3$ - $10\text{P}_2\text{O}_5$ glass.

3.3. FTIR Spectroscopy. XPS analysis was performed to verify the changes in the concentration and state of the vanadium ions in the glass due to nanocrystallization. The structural changes were expected to induce a change in the concentrations of V^{5+} and V^{4+} . Results of FTIR spectroscopy provided a direct evidence for the BO_4 restructuring observed in the XRD analysis. The infrared spectra (at 400 – 2000 cm^{-1}) of the $75\text{V}_2\text{O}_5$ - $15\text{B}_2\text{O}_3$ - $10\text{P}_2\text{O}_5$ glass annealed for 4 h and heat-treated at 275°C for different durations (1, 3, and 5 h) are shown in Figure 6. The vibration modes of the borate network were found to be active mainly in three infrared regions, as previously reported [16, 17]. The group of bands located at 1200 – 1600 cm^{-1} is attributed to the B-O bonds in the trigonal

FIGURE 5: V $2p_{3/2}$ core level spectra fitted with a single peak of V^{5+} and V^{4+} for glasses (a) annealed at 225°C and heated for crystallization at 275°C for (b) 1, (c) 3, and (d) 5 h.

TABLE 1: Peak positions, areas, and relative concentrations of V^{4+} and V^{5+} resulting from the curve fittings of the V 2p spectra of the $75V_2O_5$ - $15B_2O_3$ - $10P_2O_5$ glasses heat-treated at 275°C .

Heating process	Peak BE	Height counts	FWHM (eV)	Area	$[V^{5+}]/[V_{\text{total}}]$	$[V^{4+}]/[V_{\text{total}}]$
Annealed	517.71	3353.98	1.60	5705.38	0.9033	0.0967
	516.52	390.71	1.47	611.07		
$275^{\circ}\text{C}/1\text{ h}$	517.53	3374.83	1.45	5214.94	0.8202	0.1798
	516.64	632.89	1.70	1143.24		
$275^{\circ}\text{C}/3\text{ h}$	517.74	3275.23	1.45	5052.32	0.7823	0.2177
	516.88	802.80	1.65	1406.09		
$275^{\circ}\text{C}/5\text{ h}$	517.54	2328.67	1.58	3919.33	0.7230	0.2770
	516.80	779.33	1.81	1501.61

FIGURE 6: Infrared spectra of $75\text{V}_2\text{O}_5\text{-}15\text{B}_2\text{O}_3\text{-}10\text{P}_2\text{O}_5$ glass heat-treated at 275°C .

BO_3 units. The second group of bands, located at $800\text{--}1200\text{ cm}^{-1}$, could be ascribed to the B-O bond stretching in the tetrahedral BO_4 units. A third group of absorption bands was observed at around 600 cm^{-1} , which can be attributed to the bending of O-B-O linkages in the borate network [18, 19].

The absence of a peak at 809 cm^{-1} indicates that no boroxol ring was formed [20], which suggests that the glass system under investigation consists of randomly connected BO_3 and BO_4 groups. The absorption peaks at 1195 and 1465 cm^{-1} are related to the fundamental asymmetrical stretching vibration of the B-O bond in the trigonal BO_3 units [21, 22]. Mitigation of the slope of the absorption band indicated that B-O bond stretching in the trigonal BO_3 units occurred during heat treatment at 275°C . In addition, the absorption peak intensity at 1468 cm^{-1} (BO_3 structure) shifted to lower wave numbers ($1468\text{--}1430\text{ cm}^{-1}$) as the heat treatment was significantly reduced. The stretching vibration of the B-O bond in the tetrahedral BO_4 units appeared at $1050\text{--}900\text{ cm}^{-1}$. The absorption peak at 1019 cm^{-1} , attributed to the B-O bond stretching vibration in the tetrahedral BO_4 units, shifted to higher wave numbers ($1019\text{--}1020\text{ cm}^{-1}$) upon heat treatment at 275°C [17, 23].

From the FTIR analysis, shift of the vibrational band indicated that nanocrystallization at 275°C with increasing durations of heat treatment strengthened the BO_4 unit structure and weakened the BO_3 unit structure. This fact, coupled with the XRD analysis results, allowed us to examine the $\text{BO}_3 + \text{VO}_5(\text{V}_2\text{O}_5) \rightarrow \text{BO}_4 + \text{VO}_4(\text{VO}_2)$ structural change that occurred in the glass. This structural change affects the electrical conduction and catalytic properties of the vanadate glass.

3.4. Electrical Conductivity. The changes in the electrical conductivity of the heat-treated specimens are shown in Table 2. Electrical conductivity was increased by heat-treating the samples at 275°C and increasing the duration of the heat treatment.

The resulting conductivity value of $1.42003 \times 10^{-7}\ \Omega^{-1}$ obtained by heat treatment at 275°C for 1 h was approximately

TABLE 2: Electrical conductivity of $75\text{V}_2\text{O}_5\text{-}15\text{B}_2\text{O}_3\text{-}10\text{P}_2\text{O}_5$ glasses heat-treated at 275°C .

Heating process	Electric resistance	Electrical conductivity
Annealed	35857142.86	$0.278884E - 07$
$275^\circ\text{C}/1\text{ h}$	7042105.263	$1.42003E - 07$
$275^\circ\text{C}/3\text{ h}$	1765000	$5.66572E - 07$
$275^\circ\text{C}/5\text{ h}$	1330769.231	$7.51445E - 07$

5.1 times greater than the conductivity of the annealed glass. Furthermore, the resulting value of $7.51445 \times 10^{-7}\ \Omega^{-1}$ obtained by heat treatment at 275°C for 5 h was approximately 26.9 times greater than the conductivity of annealed glass.

Combining result of the electrical conductivity with those of the XRD and XPS analyses, it was hypothesized that the change in the electrical properties was because of the changes in the VO_5 and VO_4 structures caused by the change in the coordination number, which was due to the nanocrystallization. Electrical conductivity of this glass system is related to the metal ion value ratio C , which for vanadium-containing oxide glasses is defined as $C = [\text{V}^{4+}]/([\text{V}^{4+}] + [\text{V}^{5+}])$. According to Morinaga and Fujino [24], the electrical conductivity of vanadate glasses increases as C approaches 0.5. Heat-treating the $75\text{V}_2\text{O}_5\text{-}15\text{B}_2\text{O}_3\text{-}10\text{P}_2\text{O}_5$ glass at 275°C nanocrystallizes and strengthens the VO_2 phase while reducing the V_2O_5 phase. This indicates that the V^{5+} ions changed to V^{4+} as values of C approached 0.5. From these inferences, it can be predicted that this behavior leads to an increase in the electrical conductivity and that increasing the conduction path length, number of electronic transfer ports, and the VO_2 nanocrystalline phase contribute to this increased conductivity.

3.5. Catalytic Property. TGA results of two samples containing 20 mg of glass powder nanocrystallized at each heat treatment condition mixed with 20 mg of stearic acid or linoleic acid are shown in Figure 7 and Table 3. Linoleic acid ($\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}$) is a typical unsaturated fatty acid with two double bonds, and stearic acid ($\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$) is a typical saturated higher fatty acid with a carbon number of 18. Weight loss occurs when each fatty acid was partially converted to CO_2 gas by an oxidation reaction.

The finish temperature of weight loss, which is the temperature at which the oxidation reaction of linoleic acid and stearic acid is complete, associated with the conversion of the acid to CO_2 gas caused by crystallization due to 1 h heat treatment at 275°C , shifted to lower temperatures (356.05 to 324.15°C for linoleic acid and 378.67 to 341.75°C for stearic acid). Subsequently, the finish temperature of weight loss increases gradually by increasing the heat treatment duration. The finish temperature of samples heat-treated for 5 h was 340.96°C and 362.16°C for linoleic and stearic acids, respectively.

GC-MSD results of a sample containing 2 mg glass powder nanocrystallized at each heat treatment condition mixed with 8 mg of carbon are shown in Figure 8. Carbon

FIGURE 7: Weight loss of (a) linoleic and (b) stearic acids with $75\text{V}_2\text{O}_5\text{-}15\text{B}_2\text{O}_3\text{-}10\text{P}_2\text{O}_5$ glass heat-treated at 275°C .

TABLE 3: Weight loss of linoleic and stearic acids with $75\text{V}_2\text{O}_5\text{-}15\text{B}_2\text{O}_3\text{-}10\text{P}_2\text{O}_5$ glass heat-treated at 275°C .

Heating process	Linoleic acid		Stearic acid	
	Start temp. of weight loss	Finish temp. of weight loss	Start temp. of weight loss	Finish temp. of weight loss
Annealed	254.19	356.05	235.56	378.67
$275^\circ\text{C}/1\text{ h}$	245.24	324.15	233.23	341.75
$275^\circ\text{C}/3\text{ h}$	244.02	330.92	233.55	350.02
$275^\circ\text{C}/5\text{ h}$	244.23	340.96	233.62	362.16

converted into CO_2 gas by an oxidation reaction, and hence, the desorption intensity of CO_2 gas increases.

The sudden increase point of the desorption intensity, which is the temperature at which the oxidation reaction of carbon is complete, associated with the conversion of the carbon to CO_2 gas because of nanocrystallization after 1 h heat treatment at 275°C , shifted from 395.13°C to 281.25°C (Table 4). Thereafter, the sudden increase point of the desorption intensity gradually decreased by increasing the heat treatment duration. The sudden increase point after 5 h of heat treatment was 387.98°C .

Prior research results have shown that the V^{5+} to V^{4+} reduction reaction causes a catalytic effect in the oxidation reaction of reactants (linoleic and stearic acids and carbon), and the XRD, XPS, and FTIR analyses of the structural changes due to the glass nanocrystallization lead to the following conclusion. We hypothesize that, by nanocrystallizing a given composition of glass at 275°C , nanocrystal phases are produced and the glass structure is changed to a relatively more closed structure (see Section 3.6). It was determined that the tunneling effect, which is the electron transfer mechanism in the vanadate glass structure, becomes more active. However, as the heat treatment time became progressively longer, the catalytic effect diminished in strength. By increasing the heat treatment time, the relative amount

TABLE 4: Sudden increase point of the desorption intensity of CO_2 gas from carbon with $75\text{V}_2\text{O}_5\text{-}15\text{B}_2\text{O}_3\text{-}10\text{P}_2\text{O}_5$ glass heat-treated at 275°C .

Heating process	Sudden increase point of the desorption ($^\circ\text{C}$)
Annealed	395.15
$275^\circ\text{C}/1\text{ h}$	281.25
$275^\circ\text{C}/3\text{ h}$	376.24
$275^\circ\text{C}/5\text{ h}$	388.98

of the VO_2 phase increased while that of VO_5 decreased, changing the vanadium ion valency from V^{5+} to V^{4+} . Thus, the V^{5+} activity and the reduction reaction of V^{4+} decrease gradually, weakening the catalytic property. Therefore, glass nanocrystallization due to heat treatment creates a denser structure than annealed glass. This causes the V^{5+} to V^{4+} reduction reaction and catalytic action of the oxidation of fatty acid to become active. On the other hand, as the heat treatment time increased, the reduction reaction decreased, indicating that the catalytic effects declined gradually.

3.6. Other Properties. We examined the density and molar volume to obtain indirect evidence of the structural changes and the associated catalytic properties described above.

FIGURE 8: Desorption intensity of CO_2 gas from carbon conversion with $75\text{V}_2\text{O}_5$ - $15\text{B}_2\text{O}_3$ - $10\text{P}_2\text{O}_5$ glass heat-treated at 275°C .

FIGURE 9: Density and molar volume of $75\text{V}_2\text{O}_5$ - $15\text{B}_2\text{O}_3$ - $10\text{P}_2\text{O}_5$ glasses heat-treated at 275°C .

Looking at the changes in density and molar volume of $75\text{V}_2\text{O}_5$ - $15\text{B}_2\text{O}_3$ - $10\text{P}_2\text{O}_5$ glasses shown in Figure 9, we observe that the density greatly increased and the molar volume greatly decreased after heat treatment at 275°C . On the other hand, when the heat treatment duration was increased, the density slightly decreased and the molar volume slightly increased.

The results from Figure 9 provide indirect evidence that describes the changes in the catalytic properties. When the glass is nanocrystallized by heat treatment, its structural density is much higher compared to the annealed glass, which leads to the enhanced catalytic activity. Increasing the heat treatment duration then leads to weaker catalytic activity because the structure gradually becomes less dense.

4. Conclusions

The purpose of this study was to examine and verify the correlation between the changes in the catalytic and electrical properties and the structure due to the nanocrystallization of $75\text{V}_2\text{O}_5$ - $15\text{B}_2\text{O}_3$ - $10\text{P}_2\text{O}_5$ glass containing a mix of V^{5+} , V^{4+} , BO_4 , and BO_3 . Using various equipment of structural analysis, we conformed the $\text{BO}_3 + \text{VO}_5(\text{V}_2\text{O}_5) \rightarrow \text{BO}_4 + \text{VO}_4(\text{VO}_2)$ change in structure by nanocrystallizing and increasing the duration of heat treatment.

The changes in the catalytic properties and electrical conductivity were due to the nanocrystal structure and the state of the vanadium ions. The heat treatment used for nanocrystallization caused the electrical conductivity to increase continually; this is because the ion ratio, C value, approaches 0.5 owing to the transition of V^{5+} to V^{4+} . On the other hand, after being improved for the purpose of nanocrystallization, the catalytic effect decreased as the duration of heat treatment increased. This is because, during nanocrystallization, the glass structure is dense and the tunneling effect occurs more actively. This behavior accelerates the reaction responsible for the catalytic activity. However, by increasing the duration of heat treatment, the vanadium ion valency changes from V^{5+} to V^{4+} , and the activity of V^{5+} decreases; that is, the reduction reaction site of V^{4+} decreases gradually, causing the catalytic property to weaken. In addition, we indirectly and quantitatively confirmed the structural change through the increase in density and the decrease in molar volume due to nanocrystallization and the decrease in density and the increase in molar volume due to increasing the duration of heat treatment.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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