Structural, Optical, and Chemical Properties of Cadmium Phosphate Glasses

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ABSTRACT

In this study, we prepared cadmium phosphate glasses with various compositions, given by $x\text{CdO}-(100-x)\text{P}_2\text{O}_5$ ($x = 10-55$ mol%), and analyzed their Fourier transform infrared spectra, dissolution rate, thermal expansion coefficient, glass transition temperature, glass softening temperature, and optical band gap. We found that the thermal expansion coefficient and dissolution rate increased while the glass transition temperature and glass softening temperature decreased with increasing CdO content. These results suggest that CdO acts as a network modifier in binary phosphate glass and weakens its structure.

Key words : *Fourier transform infrared spectroscopy, Optical band gap energy, Dissolution rate, Phosphate glass, Non-bridging oxygen, Network modifier*

1. Introduction

Phosphate glasses have a number of unusual properties that have attracted attention over the years. More than a century ago, it was found that phosphate glasses have low dispersion, high refractive index, and high UV transparency when compared to silicate glasses.^{1,2)} Moreover, phosphate glasses are particularly attractive hosts because they can accommodate large concentrations of active ions without any deterioration in their useful properties. Recently, phosphate glasses with high concentrations of transition metals have been attracting considerable interest because of their semiconducting properties and optical absorption in the visible region, which results in glass coloration. Among transition metals, cadmium is used as a coloring, phase separation, and photoconductive material. Moreover, cadmium is used in quantum dot solar cells because of its high density and low binding energy. Cadmium-phosphate-based glasses have been used as matrices for the growth of cadmium selenide quantum dots; however, little is known of the structure of binary cadmium phosphate glasses. In the present study, we changed the composition of cadmium phosphate glasses represented by $x\text{CdO}-(100-x)\text{P}_2\text{O}_5$ ($x = 10-55$ mol%) and observed the chemical durability as well as structural, optical, and thermal properties of these glasses.

2. Experimental Procedure

2.1. Glass preparation

Glass samples with the composition $x\text{CdO}-(100-x)\text{P}_2\text{O}_5$ ($x = 10, 20, 30, 40, 45, 50$, and 55 mol%) were prepared using $\text{NH}_4\text{H}_2\text{PO}_4$ (Junsei Chemical Co., Japan) and CdO (Junsei Chemical Co., Japan).

All the glass samples were prepared in 45-g batches; the constituents were mixed together by grinding them repeatedly to obtain homogeneity. This mixture (45 g) was melted in an alumina crucible in an electrically heated furnace under ordinary atmospheric conditions at a temperature of 300°C for about 2 h in order to evaporate ammonia, carbonate, and water from the batch and to minimize the tendency of the glass to undergo subsequent phosphate volatilization. The temperature was then raised gradually to 1100°C and maintained at this value for 90 min to homogenize the melt. The obtained melt was quenched in a stainless-steel-plated vessel; the glass was then annealed at 500°C for 3 h to relieve mechanical stresses and to lessen the tendency of the freshly formed glass to crack.³⁾

2.2. Measurements

The amorphous nature of the samples was confirmed by X-ray diffractometry (XRD, Rigaku-Ultima IV). The thermophysical properties of the prepared glass samples were measured using a model Q400 thermal mechanical analyzer (TA Instruments) at a heating rate of $10^\circ\text{C}/\text{min}$. From the obtained curves, the linear coefficient of thermal expansion (α) of the glass samples was obtained as the mean value in the temperature range $100-300^\circ\text{C}$. The glass transition temperature (T_g) was determined from the change in the slope of the elongation vs. temperature plot. The glass soft-

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ening temperature (T_d) was obtained from the maximum of the expansion curve. The chemical durability of the glass samples was evaluated from their dissolution rates (DRs) in distilled water at 60°C. For this, glass cubes were placed in distilled water for 72 h. The DR was calculated from the expression $DR = \Delta w/S t$, where Δw is the weight loss (g), S is the sample area (cm^2) before the dissolution test, and t is the dissolution time (min)⁴. The structure of the glass samples was analyzed by Fourier transform infrared (FTIR) spectroscopy (KBr, Spectrum GX, 400–1400 cm^{-1}). The optical transmittance and absorption of all glass samples were investigated using a UV-vis spectrometer (8453, Agilent Technologies).

3. Results and Discussion

3.1. Glass-forming region

Figure 1 shows the XRD data for the prepared $x\text{CdO} - (100 - x)\text{P}_2\text{O}_5$ glasses.

Fig. 1. XRD data for $x\text{CdO} - (100 - x)\text{P}_2\text{O}_5$ glasses.

$(100 - x)\text{P}_2\text{O}_5$ glasses. It can be observed that a crystallization peak appears when the CdO content is more than 60 mol%. Moreover, a visual inspection revealed that the glasses were opaque when the CdO content was 60 mol%.

Therefore, in this paper, only cadmium concentrations in the range 10 - 55 mol% are discussed.

3.2. Structural properties

The IR spectra of the prepared $x\text{CdO} - (100 - x)\text{P}_2\text{O}_5$ glasses are shown in Fig. 2. A PO_2 asymmetric stretching vibration (V_{as}) band, PO_2 symmetric stretching vibration (V_s) band, V_{as} band for P–O–P groups, and V_s band for P–O–P groups can be observed near 1270, near 1160, near 890, and near 720 - 775 cm^{-1} , respectively.⁵ It can be observed that in the 720–775 cm^{-1} region, the wavenumber decreases gradually with increasing CdO content. On the basis of this observation, we were able to confirm that cadmium breaks P–O–P bonds and increases the number of non-bridging oxygen (NBO) atoms⁶⁻⁹. Further, it can be observed that the small peak near 1200 cm^{-1} becomes sharper with increasing CdO content. The reason for this is that the breakage of P–O–P bonds results in the occurrence of symmetric and asymmetric stretching vibrations of PO_2 . Thus, we can conclude that CdO acts as a network modifier in binary phosphate glasses.

Van Wazer explained the structure of P_2O_5 in phosphate glass using Q terminology¹⁰. Short-range structures of binary phosphate glasses can be described by the type and concentration of $[\text{PO}_4]$ species and can be denoted by Q^n ($0 \leq n \leq 3$), where n is the number of bridging oxygen atoms per tetrahedron. Fig. 3 shows Q^0 , Q^1 , Q^2 , and Q^3 (number of bridging oxygen atoms: 0, 1, 2, and 3, respectively).

In binary phosphate glasses, the fractions of Q^2 and Q^3 are given by the following simple expression:

$$x\text{R}_2\text{O}(\text{or R'O}) - (1 - x)\text{P}_2\text{O}_5,$$

Fig. 2. Infrared spectra of $x\text{CdO} - (100 - x)\text{P}_2\text{O}_5$ glasses.

Fig. 3. Structure of phosphate glass.

Fig. 4. Theoretical values of number of bridging oxygen atoms.

$$f(Q^2) = \frac{x}{1-x}, f(Q^3) = \frac{1-2x}{1-x}, x \leq 50 \quad (1)$$

According to this expression, Q^3 decreases and Q^2 increases with increasing CdO content. When R_2O is more than 50 mol%, the fractions of Q^1 and Q^2 are given by the following expression:

$$xR_2O(\text{or } R'O) - (1-x)P_2O_5, \\ f(Q^2) = \frac{2-3x}{1-x}, f(Q^1) = \frac{2x-1}{1-x}, 50 \leq x \leq 67 \quad (2)$$

It is possible to know that Q^2 decreases and Q^1 increases with increasing CdO content through Eq. (2).

Figure 4 shows the theoretically calculated values of the number of bridging oxygen atoms. On the basis of these results, we can conclude that increasing CdO content increases the number of NBO atoms. As a result, the glass structure is weakened by the presence of cadmium ions.

3.3. Chemical durability

Generally, the DR of glass increases when the glass structure becomes weaker.^{11,12)} Fig. 5 shows that the DR increases consistently with increasing CdO content. This is attributed to the replacement of P–O–P bonds by P–O–Cd

Fig. 5. Variations in dissolution rate of $x\text{CdO} - (100 - x)\text{P}_2\text{O}_5$ glasses.

bonds; this replacement is accompanied by a decrease in chemical durability. These findings prove that the bonding forces inside the structural network weaken as a result of the formation of P–O–Cd bonds. This is because the strength of the Cd–O bond (236 kcal/mol) is much lower than that of the P–O bond (599 kcal/mol). Generally, a glass structure consists of both ionic and covalent bonding. However, as shown in Fig. 5, there is a rapid increase in DR when the CdO content is more than 40 mol%. The reason for this result may be ascribed to the exponential increase of ionic bonding when CdO content is more than 40 mol%. Increase of ionic bonding weakens the glass structure and rapidly decreases the chemical durability. Rapid change in property when CdO content is more than 40 mol% was further confirmed through analysis of the optical property.

3.4. Optical properties

Figure 6 shows the optical energy band gap of the prepared glasses as measured by UV-vis spectroscopy. The optical energy band gap was calculated using the absorption coefficient of the glasses. The Lambert–Beer equation ($I/I_0 = e^{-\alpha d}$) and Tauc's equation ($\alpha(\nu)h\nu \approx (h\nu - E_g)^n$) were used¹³⁾, and the calculated values were plotted using an indirect method. An increase in the CdO content resulted in the optical edge shifting to the left and the optical band gap decreasing. This is because the donor center is increased by NBO atoms, thereby leading to a decrease in the optical

Fig. 6. Variations in optical band gap of $x\text{CdO}-(100-x)\text{P}_2\text{O}_5$ glasses.

band gap. Further, a rapid decrease in the band gap energy was observed when the CdO content was more than 40%. This result is similar to the results of the analysis of the chemical property. Abrupt changes in the optical band gap energy mean that NBO atoms increase rapidly when CdO content is more than 40 mol%. In general, ionic bonding increases when NBO atoms that can participate in ionic bonding increase¹⁴. For these reasons, it is expected that covalent bonding decreases sharply and ionic bonding begins to increase radically when CdO content is more than 40 mol%.

3.5. Thermal properties

Figure 7 shows the dependences of α , T_g , and T_d on the CdO content of the prepared glasses. It can be observed that α increases, whereas T_g and T_d decrease with increasing CdO content. In general, α increases when the glass structure becomes weaker. On the basis of Fig. 7, it can be concluded that the glass structure is weakened by the presence of CdO.

4. Conclusion

The purpose of this study was to identify vitrification areas in cadmium phosphate glasses and analyze the structural characteristics, chemical durability, and optical and thermal properties of these glasses. It was found that increasing the CdO content resulted in the breakage of P–O–P bonds and creation of NBO atoms. An increase in the number of NBO atoms weakened the glass structure. Further, increasing the CdO content also reduced the chemical durability, as well as the T_g and T_d values of the glasses. An increase in the number of NBO atoms reduced the optical band gap energy of the glasses. On the basis of the results obtained in this study, we can conclude that CdO acts as a network modifier in binary phosphate glasses and weakens its structure. In addition, it can be deduced that ionic bonding increases and covalent bonding decreases when the CdO

Fig. 7. Variations in thermal expansion coefficient, glass transition temperature, and glass softening temperature of $x\text{CdO}-(100-x)\text{P}_2\text{O}_5$ glasses.

content is more than 40 mol% through chemical and optical properties. However, this study did not involve sufficient quantitative investigation of ionic and covalent bonding of Cd–O, an issue that needs to be addressed in future research.

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