Materials Characterization 111 (2016) 177–182

Contents lists available at ScienceDirect

Materials Characterization

journal homepage: www.elsevier.com/locate/matchar

Physical and absorption properties of titanium nanoparticles incorporated into zinc magnesium phosphate glass

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ARTICLE INFO

Article history:
Received 7 July 2015
Received in revised form 27 November 2015
Accepted 30 November 2015
Available online 2 December 2015

Keywords:
Amorphous state
Optical band gap
Physical properties
Titanium nanoparticles

ABSTRACT

We report the influences of Titania (TiO_2) nanoparticles (NPs) on the physical and optical properties of melt quench synthesized zinc magnesium phosphate glasses. Five glass samples with composition $(42 - x)P_2O_5$–$50ZnO$–$8MgO$–$xTiO_2$, where $x = 0, 1, 2, 3, 4$ mol% are prepared and characterized. XRD pattern verified the amorphous nature of all samples. TEM images manifested the growth of Ti NPs of average size ≈ 5.78 nm. TiO_2 NP concentration dependent variation in the physical properties including glass density, molar volume, molar refractivity, electronic polarizability and ionic packing density are determined. The values of glass refractive indices, density and ionic packing density are increased with the increase of TiO_2 NP contents. Conversely, the Urbach energy, direct and indirect optical band gap are found to decrease with the increase of TiO_2 NP concentration. These glass compositions may be potential for various solid state devices including laser.

1. Introduction

Certainly, phosphate glasses are prospective over conventional silicate and borate systems due to their unique physical properties such as high temperatures expansion coefficient, low melting and transition temperatures, lower indices of refraction and prominent ultra-violet transmission. Recently, intensive research on ZnO–P_2O_5, MgO–P_2O_5 and ZnO–MgO–P_2O_5 glasses displaying their superior structural, physical, thermal and optical properties made them potential for diverse device applications [1–3]. Khor and co-workers [1] examined the physical and optical properties of simultaneous admixture of MgO and ZnO into the phosphate compositions and demonstrated their strong influenced on overall properties.

Lately, TiO_2 NPs received special attention due to its several advantages properties and potential benefits including low cost, chemical stability, non-toxicity and, high reactivity under UV light irradiation [4]. Moreover, TiO_2 is a wide band gap (≈3.2 eV) semiconductor [5,6]. Generally, TiO_2 NPs are widely used for photovoltaic cells, electro-chromic materials, photo-catalysis, self-cleaning glass and waste water treatment [5,7]. The reconstruction of the TiO_2 occurs upon prolonged heating, where the titanium ions usually exist in Ti^{4+} state. These Ti^{4+} ions form TiO_4, TiO_6 and rarely TiO_5 (comprising of trigonal bipyramids) structural units in the glass network [8,9]. However, some reports acknowledged the existence of Ti^{3+} valence state in the glass matrices [10,11]. According to Diebold [12], slightly defective TiO_2 surface reveals weak feature due to the presence of small amounts of Ti^{3+} defects when heated to 1000 K.

The goal of this study is to examine the effects of varying concentrations of TiO_2 NPs on the physical and optical properties of zinc magnesium phosphate amorphous matrix. Ti NP mediated emergent physical and optical properties of ZnO–MgO–P_2O_5 glass system are inspected. Results are analyzed, compared and discussed.

2. Experimental

The nominal glass compositions with their codes are listed in Table 1. About 20 g batch with analytical grade glass constituents of P_2O_5 (purity 98.94%), ZnO (purity 99%), MgO (99%) and TiO_2 (purity 99.7%) in powder form are well-mixed and melted in alumina crucibles at 1100 °C for 2 h in an electrical furnace so that a homogeneously mixed melt is obtained. The melt is then transferred to an annealing furnace and poured on the brass mold before being annealed at 400 °C for 3 h to reduce the mechanical stress that causes embrittlement [13]. The vitreous/amorphous state of the prepared samples is examined by X-ray diffraction (XRD) measurement on a Siemen Diffractometer that used Cu-Kα ($\lambda = 1.54$ Å) as radiation source. Relatively fine glass powder is placed in a sample holder and scanned from $2\theta = 10$–$80°$ with a step of 0.50° at running voltage of 30 kV and current 20 mA. The presence of NPs in the glass matrix is detected using a transmission electron microscope (TEM, Philips CM12), which operated at 200 kV with Dock version 3.2 image analyzer. Specimens for TEM are prepared by dispersing the powder in acetone via ultrasonic bath. The solution is then placed onto copper grid and allowed to dry before got ready for characterization. TEM images are analyzed to determine the NP sizes, shapes, and distribution in the glass matrix. In addition, the Energy Dispersive of X-Ray (EDX) analysis is used to analyze the sample composition.

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http://dx.doi.org/10.1016/j.matchar.2015.11.030
1044-5803/

Table 1
Chemical compositions of the synthesized glasses with codes.

Sample code	Chemical composition (mol.%)			
	P_2O_5	MgO	ZnO	TiO_2
S1	42	8	50	0
S2	41	8	50	1
S3	40	8	50	2
S4	39	8	50	3
S5	38	8	50	4

Room temperature UV–Vis–NIR measurements in the wavelength range of 200–700 nm (Shimadzu 3101PC UV–Vis–NIR scanning spectrophotometer) are carried out on well-polished (up to 1200 μm grid size using diamond paste), highly transparent and shiny glass samples of thickness 2 mm. The absorption spectra are further exploited to evaluate optical band gaps, Urbach energies, and refractive indices of all prepared samples. The photon energy ($h\nu$) dependent optical absorption coefficient, $\alpha(\nu)$ near the absorption band edge yields,

$$\alpha(\nu) = \frac{2.303A}{d} \tag{1}$$

where A is the absorbance and d is the thickness of the sample.

Following Davis and Mott [14], for amorphous and semiconducting materials the values of $\alpha(\nu)$ as a function of photon energy can be calculated from,

$$\alpha(\nu) = \frac{C(h\nu - E_{opt})^n}{h\nu} \tag{2}$$

where C is a constant, E_{opt} is the optical band gap energy with $n = 2$ for indirect transition and $n = 1/2$ for direct transition.

The Urbach energy (ΔE) that characterizes the extent of the exponential tail of the absorption edge can be written as

$$\alpha(\nu) = B\exp\left(\frac{h\nu}{\Delta E}\right) \tag{3}$$

where B is a constant. The Urbach energy measures the width of the band tails of the localized states.

The refractive index (n) is related to the indirect optical band gap energy E^I_{opt} via

$$\frac{n^2-1}{n^2+2} = 1-\sqrt{\frac{E^I_{opt}}{20}}. \tag{4}$$

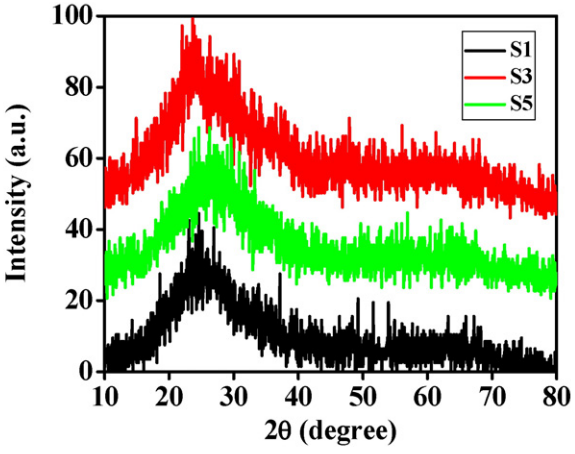

Fig. 1. Typical XRD pattern for S1, S3 and S5 glass samples.

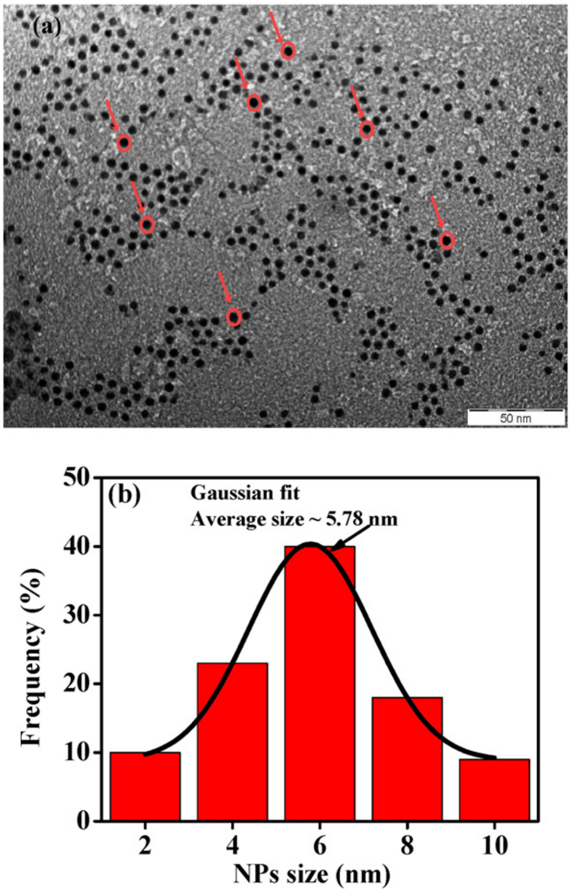

Fig. 2. (a) TEM image of S5; (b) size distribution of TiO_2 NPs in S5.

The density (ρ in g/cm^3) of glass samples is determined via Archimedes method with toluene (insoluble in water and does not react with glass samples) as immersion liquid. The estimated error in density measurement is $\approx \pm 0.001$ g/cm^3. The sample weight in the air and within the immersion liquid is measured using a digital balance. Glass density is calculated using,

$$\rho = \rho_T \frac{W_A}{W_A - W_L} \tag{5}$$

where ρ_T is the density of toluene (0.8669 g/cm^3), W_A and W_L are the weight of the sample in the air and liquid respectively.

The molar volume (V_m in cm^3/mol) is calculated from

$$V_m = \sum \frac{n_i m_i}{\rho} \tag{6}$$

where n_i and m_i denote the molar fraction and molecular weight of ith component, respectively. The molar refractivity (R_m), the electronic polarizability (α_e) and the ionic packing density (V_t) are determined from the value of molar volume using the following relations:

$$R_m = \frac{n^2-1}{n^2+2}(V_m) \tag{7}$$

$$\alpha_m = \left(\frac{3}{4\pi N_a}\right) R_m \tag{8}$$

$$V_t = (4/3\pi)\sum_i (r_i^3 n_i)/V_m \tag{9}$$

$$N = (n_p N_a \rho)/M \tag{10}$$