*Proceedings of International Conference on Technology and Social Science 2017*
*Invited Paper*

# Fabrication and Characterization of $Pr^{3+}$ Doped Zinc Barium Tellurite Glasses

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**Key word**: Tellurite glasses, $Pr^{3+}$-doped glasses, zinc barium glasses

**Abstract**. $Pr^{3+}$ doped zinc barium tellurite glasses (ZBaT: ZnO – BaO – $TeO_2$) were prepared by melt quenching technique. The physical, optical and photoluminescence studies are characterized through density, molar volume, absorption and photoluminescence spectrum measurement, respectively. The results showed that the density of the glasses increased whereas the molar volume decreased with increasing of $Pr_2O_3$ concentrations.The optical absorption spectra of glasses were measured in the wavelength range of 200 – 2,500 nm. The intensity of all absorption bands increased with increasing of $Pr_2O_3$ contents. In addition, the photoluminescence properties of $Pr^{3+}$ doped ZnO – BaO – $TeO_2$ glass system were carried out using excitation wavelengths of 445 nm. Seven luminescence bands were observed at 563 nm ($^3P_1 \rightarrow {}^3H_5$), 544 nm ($^3P_0 \rightarrow {}^3H_5$), 615 nm ($^3P_0 \rightarrow {}^3H_6$),645 nm ($^3P_0 \rightarrow {}^3F_2$), 684 nm ($^3P_0 \rightarrow {}^3F_2$), 708 nm ($^3P_0 \rightarrow {}^3F_3$) and 730 nm ($^3P_0 \rightarrow {}^3F_4$) wavelength. The intense red emission was found at the band of 645 nm.

## 1. Introduction

Among motivated studies of glassy materials, tellurite based glasses drew much interest because of their unique properties such as high dielectric constant and excellent transmission in the visible as well as infrared (IR) wavelength regions, good mechanical strength and chemical durability [1-4]. These glasses also possess higher refractive index, which is approximately in the range of 2.0–2.5 [5-8], and their low melting temperature (about 800 °C) contributes to the high possibility of stable glass forming using a conventional melt quenching method [4]. Pure tellurium oxide cannot form glass by itself; it needs another element known as a glass modifier such as alkali metal, alkaline earth metal oxide and transition metal oxide (TMO) to improve the network connectivity to produce a stable tellurite glass [9,10] with increasing of non-bridging oxygen [9]. In fact, it is believed that the properties of oxide glasses strongly depend on the nature and the concentration of the constituent oxides [11]. Optical spectroscopy is an important tool to study the nature of glasses for the past many years. Investigation of the absorption and luminescence properties of rare earth (RE) doped luminescent materials have found diverse applications in the fields of lasers, telecommunications, optical fiber cables, solar concentrators, optical detectors and the production of wide variety for optical components (as windows, prisms, beam splitters, etc.,). In order to identify new optical devices for specific applications with enhanced performance, active work is being carried out by selecting the appropriate new hosts doped with RE–ions. Among thr RE ions, $Pr^{3+}$ holds the promising luminescence properties at specific near-infrared wavelength bands within the expanded low-loss window. In glass hosts, tellurite glasses have been demonstrated to be a favorable material for optical lasers and amplifiers owing to their good thermal stability, excellent mechanical strength and outstanding ion-exchangeability.

The present work reports the physical, optical and luminescence properties of $Pr^{3+}$ ion in zinc–barium–tellurite glasses. On the basis of the density, molar volume, refractive index, absorption spectra, luminescence and $Pr^{3+}$ energy-transition analysis has been applied to investigate the phenomena.

## 2. Experiment

The melt quenching preparation of zinc barium tellurite (ZBaT) glass doped with $Pr^{3+}$ were based on (80-x)$TeO_2$–15ZnO–5BaO–x$Pr_2O_3$ formular. Concentration of $Pr_2O_3$ was varied between x = 0.00 – 2.00 mol% (see Table 1). All component powders of the total chemical weight 15 g of batch materials were thoroughly mixed and crushed in an agate mortar. Then, the homogeneous mixture was transferred into an alumina crucible. Glass samples in alumina crucibles were melted in an electrical furnace at 850°C for 1 hour. These melting components were quenched between the graphite plates. These obtained glasses were all annealed at 350 °C for 3 hours before cooled down to room temperature to remove thermal strains in the glasses. Finally, glass samples were cut and then finely polished to a dimension of 1.0 cm × 1.5 cm × 0.3 cm.

Table 1. Fractional doping of $Pr_2O_3$ for zinc barium tellurite glasses.

| **Samples no.** | **$Pr_2O_3$ (mol%)** | **Glass composition** |
|---|---|---|
| 1 | 0.50 | 79.50$TeO_2$–15ZnO–5BaO–0.50$Pr_2O_3$ |
| 2 | 1.00 | 79.00$TeO_2$–15ZnO–5BaO–1.00 $Pr_2O_3$ |
| 3 | 1.50 | 78.50$TeO_2$–15ZnO–5BaO–1.50 $Pr_2O_3$ |
| 4 | 2.00 | 78.00$TeO_2$–15ZnO–5BaO–2.00 $Pr_2O_3$ |

The densities (ρ) were measured by Archimedes method using xylene as an immersion liquid. The optical absorption spectra of glass samples were recorded in the ultraviolet (UV), visible light (VIS) and near-infrared (NIR) regions in the range of 200 – 2,500 nm by using a UV–3600 Shimadzu UV–VIS–NIR spectrophotometer. The luminescence spectra measurements were carried out using Cary Eclipse fluorescence spectrophotometer with 445 nm excitation of a xenon flash lamp.

## 3. Result and Discussion

Table 2.The physical properties of $Pr_2O_3$ doped zinc barium tellurite glasses.

| **Concentration of $Pr_2O_3$** | **Density ($g/cm^3$)** | **Total molecular weight (g/mol)** | **Molar Volume ($cm^3/mol$)** |
|---|---|---|---|
| 0.5 | 5.1947 | 150.6037 | 28.9919 |
| 1.0 | 5.2516 | 151.4548 | 28.8396 |
| 1.5 | 5.2888 | 152.3059 | 28.7979 |
| 2.0 | 5.3291 | 153.1570 | 28.7394 |

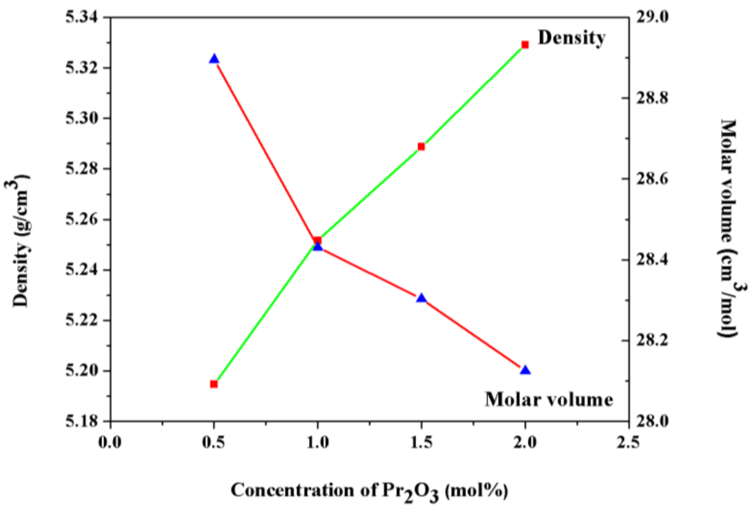


Figure.1. The density and molar volume of ZBaT glasses doped with $Pr^{3+}$ion.

The densities and molar volumes of the investigated ZBaT glasses are shown in Fig.1. The density (ρ) was increased with an increase in $Pr_2O_3$ concentration. The molar volume ($V_M$) depends on the density of glasses and as expected in the present case, it follows a trend opposite to density. The molar volumes of glasses were decreased with increasing of $Pr_2O_3$ concentration, reflecting that the glass structure was more compact with higher concentration of $Pr_2O_3$, which leads to decrease the average atomic distance. The values of density are in the range of 5.19 to 5.32 g/cm$^3$ while their molar volumes are in the range of 28.99 to 28.73 cm$^3$/mol.

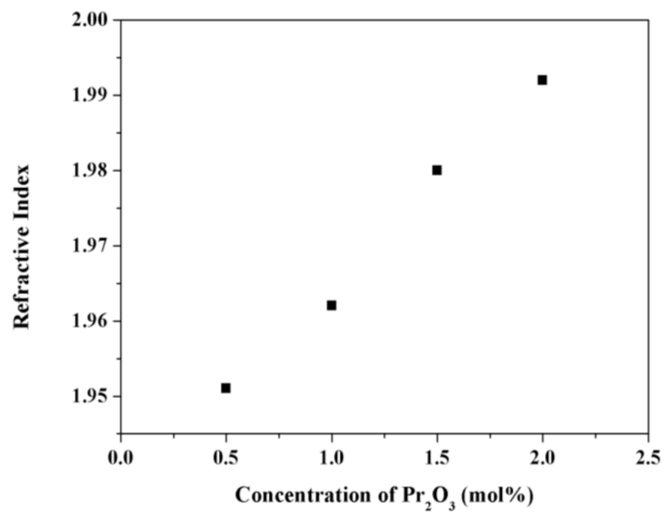


Figure 2. The refractive index of ZBaT glasses doped with $Pr^{3+}$ion.

The refractive index of glass increase linearly with increasing of $Pr_2O_3$ concentration as shown in Fig. 2. Change of refractive index proceed slightly that corresponds to the addition of glass density with more $Pr_2O_3$ concentration.

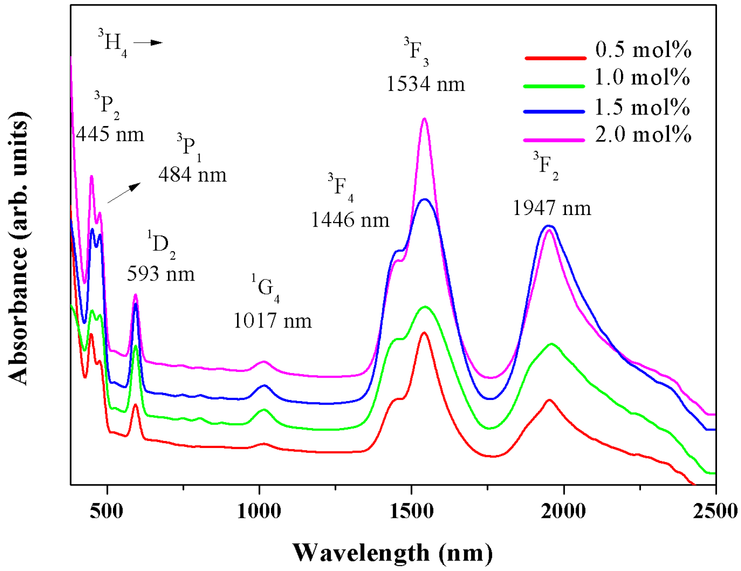


Figure 3. The optical absorption spectra of ZBaT glasses doped with $Pr^{3+}$ion.

The optical absorption spectra at room temperature were measured covering the wavelength of 200 – 2,500 nm using UV–VIS–NIR spectrophotometer (UV–3600, Shimadzu). The absorption spectra of $Pr^{3+}$ doped zinc barium tellurite glasses in the UV–VIS–NIR are shown in Fig. 3. The spectra obtained for all $Pr^{3+}$doped zinc barium tellurite glasses are similar in nature except for the band intensities. It is clearly observed that the absorption intensity of the absorption band increases with the increase of $Pr_2O_3$ concentration. The absorption bands of $Pr^{3+}$ represent the transitions from the ground state $^3H_4$ to various excited states such as $^3P_2$ (445 nm), $^3P_1$(484 nm),$^1D_2$ (593 nm), $^1G_4$(1,017 nm), $^3F_4$(1,446 nm), $^3F_3$(1,534 nm) and$^3F_2$ (1,947 nm).

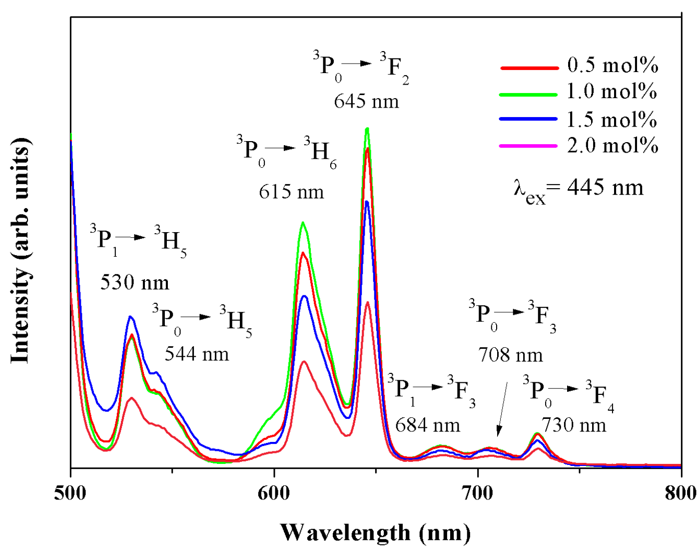


Figure 4. The emission spectra ($\lambda_{ex}$ = 445 nm) of ZBaT glasses doped with $Pr^{3+}$ion.

Fig. 4. shows the luminescence spectra of $Pr^{3+}$ doped zinc barium tellurite glasses using 445 nm excitation wavelengths from a xenon flash lamp. The spectra consist of seven emission bands in green, orange, red and NIR regions centered at 530, 544, 615, 645, 684, 708 and 730 nm corresponding to the transitions $^3P_1 \rightarrow ^3H_5$, $^3P_0 \rightarrow ^3H_5$, $^3P_0 \rightarrow ^3H_6$, $^3P_0 \rightarrow ^3F_2$, $^3P_1 \rightarrow ^3F_3$, $^3P_0 \rightarrow ^3F_3$ and $^3P_0 \rightarrow ^3F_4$ respectively. The emission intensity of luminescence materials is known to be dependent on the doping concentration of luminescent ions. It is also noticed that the relative intensity of $^3P_0 \rightarrow ^3F_2$ transition of $Pr^{3+}$ is varied as a function of $Pr^{3+}$ concentration (x = 0.5, 1.0, 1.5 and 2.0 mol%). The maximum luminescence intensity was observed at x = 1.0 mol% of $Pr_2O_3$. The decrease in emission intensities with the increase of 0.5,1.5 and 2.0 mol% of $Pr_2O_3$ concentration is due to the rise in non-radiative decay channels, which are enhanced due to the concentration quenching effect. If the concentration of an activator is higher than an appropriate value (typically several mol%), the emission intensity will be decreased. Fig. 5. shows the partial energy level diagram representing the energy level scheme involved in the emission mechanism in $Pr^{3+}$ ion in the ZBaT glasses.

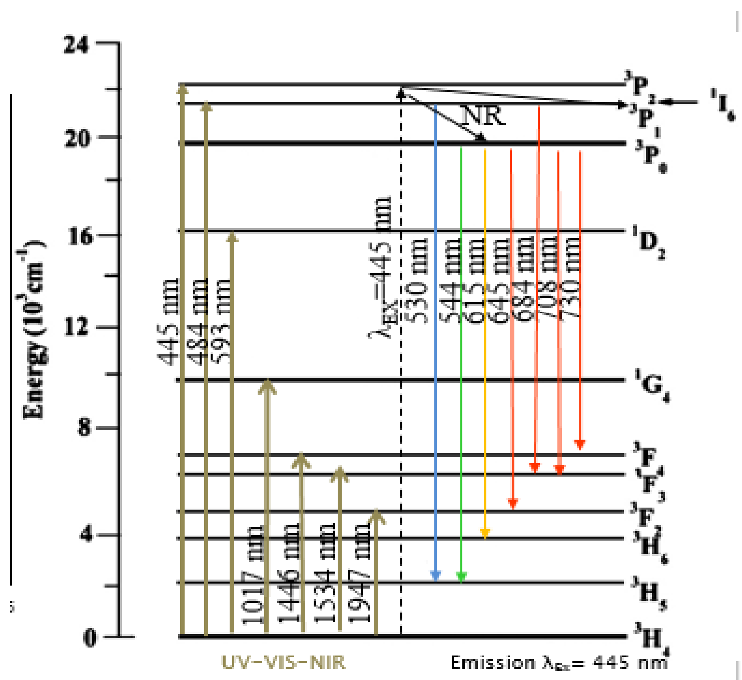


Figure 5. Partial energy level diagram showing the possible emission transitions of $Pr^{3+}$ ion in ZBaT glasses system.

## 4. Conclusion

The $Pr^{3+}$ doped zinc barium tellurite glasses were prepared at the various doping concentration of $Pr_2O_3$ and characterized for their physical, optical and luminescence properties. The density and refractive index of glass samples were increased with an increasing of $Pr_2O_3$ concentration. While, the molar volumes of glasses were decreased with $Pr_2O_3$ concentration increase. The intensities of absorption bands increase with the increase of $Pr_2O_3$ content. Glass performs the strongest emission of visible light with 645 nm, corresponding to $^3P_0 \rightarrow ^3F_2$ transition, under excitation with 445 nm wavelength. The maximum luminescence intensity of the 645 nm emission was observed in glass with x = 1.0 mol% of $Pr_2O_3$.

**Acknowledgements**

The authors would like to thank National Research Council of Thailand (NRCT) for partially support of this research.

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