

EFFECT OF PRASEODYMIUM ION CONCENTRATION ON OPTICAL AND LUMINESCENCE PROPERTIES OF TELLURITE GLASSES PRODUCED BY MELT-QUENCHING TECHNIQUE

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Received: May 07, 2023; Revised: July 04, 2023; Accepted: August 18, 2023

Abstract

Tellurite glasses with different concentration of praseodymium (Pr^{3+}) ion was produced by melt-quenching technique. The effect of Pr^{3+} concentration on optical and luminescence properties was presented. The optical absorption spectra of Pr^{3+} ions in glasses were recorded in the UV-VIS-NIR region. By using the integrated absorption spectrum, the Judd-ofelt parameters for Pr^{3+} ions were derived. The Judd-Ofelt theory was used to calculate the radiative transition probability, stimulated emission cross-section, and branching ratio of the glasses. These findings support the use of these glasses in laser and other optical device applications.

Keywords: Branching ratio; luminescence; praseodymium ion; tellurite glasses

Introduction

Tellurite glasses have unique optical and physical properties, including high refractive index, low melting point, and high non-linear optical properties. Tellurite glasses are generally transparent and colorless, but their properties can be modified by adding other metal oxides to the mixture. The addition of rare earth elements such as erbium and ytterbium can increase their luminescence and make them suitable for use in fiber-optic amplifiers (Aziz *et al.*, 2009; Tagiara *et al.*, 2017; Yasaka *et al.*, 2022).

Zinc fluoride (ZnF_2) glass is a specialized type of glass that offers several benefits in various applications. Here are some of the benefits of zinc fluoride glass: high transmittance, low dispersion, chemical stability, thermal stability, high refractive index, low absorption and high strength (Shaharuddin *et al.*, 2008; Neethish *et al.*, 2021).

Praseodymium (Pr^{3+}) ion-doped glasses have attracted considerable attention in recent years due to their unique optical properties. Pr^{3+} ions have

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broad absorption and emission spectra in the visible and near-infrared regions, making them ideal for use in various optical applications. Moreover, Pr³⁺ ion-doped glasses exhibit high luminescence efficiencies, making them useful for developing advanced optical devices with high sensitivity and precision. Due to their exceptional properties, Pr³⁺ ion-doped glasses have potential applications in various fields, including telecommunications, biomedical imaging, and environmental sensing (Rao *et al.*, 2018; Rajaramakrishna *et al.*, 2019).

Experiment

Tellurite glasses doped with different concentrations of Praseodymium (Pr³⁺) ions, (55-x)TeO₂-10ZnF₂-35BaO-xPr₂O₃, x = 0.05, 0.10, 0.50, 1.00, 1.50, and 2.00 mol% were prepared with analytical grade TeO₂, ZnF₂, BaO, and Pr₂O₃ with high purity up to 99.99% using the melt-quenching technique at 950°C and hold for 1 h following the procedures described in previous work (Yasaka *et al.*, 2023). The density of the object can then be found by the Archimedes principle. The molar volume of the glass sample can be calculated by dividing the volume of the sample by the number of moles of the sample. The number of moles of the sample can be calculated using its mass and molar mass. The optical and luminescence properties of the Pr³⁺ ion-doped glasses were recorded in the ultraviolet-visible-near-infrared (UV-VIS-NIR) region using a spectrophotometer. The luminescence spectra were recorded using a spectrofluorometer. The Judd-Ofelt theory was used to calculate the Judd-Ofelt parameters for Pr³⁺ ions in the glasses. The integrated absorption spectrum was used to derive the Judd-Ofelt parameters, which are essential for calculating the radiative transition probability, stimulated emission cross-section, and branching ratio of the glasses (Goldner and Auzel, 1996).

Result and Discussion

Physical Properties

The Table 1 was observed lack of trend in density and linear trend in molar volume of the tellurite glasses with increasing concentration

of Pr³⁺ ions suggests that the addition of Pr³⁺ ions has a significant effect on the glass structure and properties, leading to an expansion of the glass volume. In other words, Pr³⁺ acts as an intermediate. These findings provide valuable insights into the role of rare earth ions in glass properties and suggest potential applications for these glasses in various fields. Further studies are needed to explore the specific mechanisms by which Pr³⁺ ions affect the glass properties and to optimize the glass composition for specific applications.

Optical Properties

The optical absorption spectra of Pr³⁺ ions in glasses were recorded in the UV-VIS-NIR region in the wavelength range of 250-2,500 nm (Figure 1), the results show 8 peaks of Pr³⁺ characteristic peak at the following transition states (from the ³H₄ to high states) (Rai and Mohanty, 2012). The observation of 8 peaks in the optical absorption spectra of Pr³⁺ ions in the Tellurite glasses suggests that the Pr³⁺ ions occupy different energy levels in the glass matrix, leading to distinct absorption features at different wavelengths. The transitions from the ³H₄ ground state to higher energy states are responsible for the observed peaks in the absorption spectra, with each peak corresponding to a specific energy level and transition pathway.

Photoluminescence Properties

The Figure 2 Show the excitation spectra of Pr³⁺ doped BaO-ZnF₂ tellurite glasses, showing 3

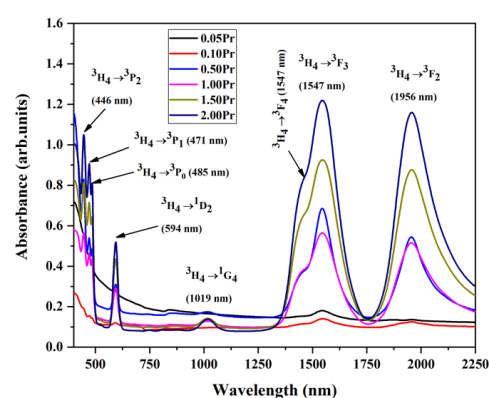


Figure 1. The absorption spectra of Pr³⁺-doped BaO-ZnF₂ tellurite glasses

Table 1. Physical Properties of Pr³⁺-doped BaO-ZnF₂ tellurite glasses

Measurement	Glass initials					
	0.05 Pr	0.10 Pr	0.50 Pr	1.00 Pr	1.50 Pr	2.00 Pr
Molar weight (g/mol)	151.8667	151.9518	152.6327	153.4837	154.3348	155.1859
Density (g/cm ³)	5.2543	5.2687	5.2664	5.2602	5.2784	5.2580
Molar volume (cm ³ /mol)	28.9034	28.8407	28.9821	29.1782	29.2390	29.5144

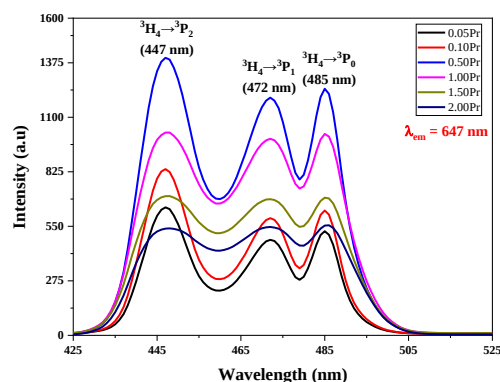


Figure 2. The excitation spectra of Pr^{3+} -doped BaO-ZnF₂ tellurite glasses

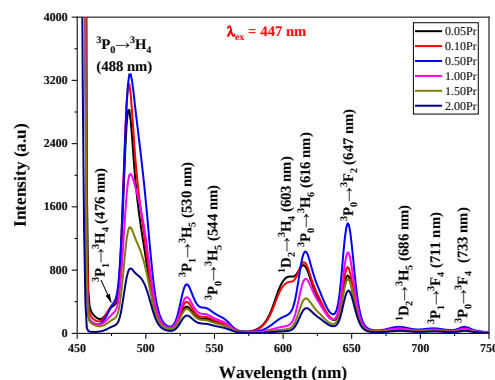


Figure 3. The emission spectra ($\lambda_{\text{ex}} = 447 \text{ nm}$) of Pr^{3+} -doped BaO-ZnF₂ tellurite glasses

Table 2. Oscillator strength calculated and experimental ($\times 10^{-6}$) and Judd-Ofelt parameter values ($\times 10^{-20} \text{ cm}^2$) of 0.5 mol% Pr^{3+} -doped BaO-ZnF₂ tellurite glasses

Transition	λ_{abs} (nm)	E_{exp} (cm^{-1})	Oscillator Strength	
			f_{exp}	f_{cal}
$^3\text{H}_4 \rightarrow ^3\text{P}_1$	476	21231	1.2690	2.6151
$^3\text{H}_4 \rightarrow ^3\text{P}_0$	485	20619	1.2346	2.5709
$^3\text{H}_4 \rightarrow ^1\text{D}_2$	594	16835	1.3347	0.5666
$^3\text{H}_4 \rightarrow ^1\text{G}_4$	1019	9814	0.3228	0.1580
$^3\text{H}_4 \rightarrow ^3\text{F}_4$	1447	6911	0.7448	1.6172
$^3\text{H}_4 \rightarrow ^3\text{F}_3$	1547	6464	4.1154	3.5289
$^3\text{H}_4 \rightarrow ^3\text{F}_2$	1956	5112	2.4050	2.4423
δ_{rms}			0.85	
Ω_2			1.5745	
Ω_4			4.1289	
Ω_6			2.2749	

peaks at 447 nm, 472 nm, and 485 nm, are indicative of the different excitation pathways available to the Pr^{3+} ions in the glass matrix. These peaks correspond to the absorption of photons of different energies, which in turn excite the Pr^{3+} ions to higher energy states. The fact that all three peaks have almost the same intensity values indicates that the excitation of the Pr^{3+} ions in the glass is not dominated by any one particular pathway. Instead, the Pr^{3+} ions are excited to different energy levels through a combination of absorption pathways, resulting in similar intensity values for each peak.

The excitation peaks at 447 nm were found to be effective in exciting the Pr^{3+} ions in the glass sample. The resulting emission peaks were observed at multiple wavelengths, ranging from 476 to 733 nm. These emissions spectra (Figure 3) correspond to different transition states of Pr^{3+} ions from the excited state to the ground state. The highest emission peak was observed at 488 nm, indicating that this transition state has the highest radiative transition probability. The intensity of the emission peaks increases with increasing concentration of Pr^{3+}

ions up to 0.5 mol%, after which it starts to decrease due to concentration quenching.

In the Table 2, the calculated oscillator strengths (f_{cal}) are generally higher than the experimental values (f_{exp}), indicating that the Judd-Ofelt theory used to calculate f_{cal} may have overestimated the transition probabilities. However, the trend in the calculated values still matches the trend in the experimental data, which suggests that the Judd-Ofelt theory can still provide valuable insights into the spectroscopic properties of Pr^{3+} ions in tellurite glasses. Overall, the comparison between f_{exp} and f_{cal} in this study indicates that the Judd-Ofelt theory can provide reasonable predictions of the optical properties of rare earth ions in glasses.

The values of Ω_2 , Ω_4 , and Ω_6 indicate that the Pr^{3+} ions have a strong interaction with the surrounding glass matrix, leading to enhanced luminescence properties. From the Table 3, we can see the radiative transition probabilities and experimental and calculated branching ratios for different transitions of Pr^{3+} ions in the glass sample.

Table 3. Radiative properties of 0.5 mol% Pr³⁺-doped BaO-ZnF₂ tellurite glasses

Transition	λ_p (nm)	$\Delta\lambda_{eff}$ (nm)	A_R (s ⁻¹)	$\sigma_e(\lambda_p) (\times 10^{-20})$ (cm ²)	β_R	
					Exp	Cal
³ P ₀ → ³ H ₄	488	20,492	16,811.81	6.4015	0.5925	0.6149
³ P ₁ → ³ H ₅	530	18,868	0.00	0.0000	0.0743	0.0000
³ P ₀ → ³ H ₆	616	16,233	1,965.57	1.9630	0.1797	0.0719
³ P ₀ → ³ F ₂	647	15,456	4,682.11	8.9840	0.1534	0.1713

The transition from ³P₀ to ³H₄ at a wavelength of 488 nm has the highest radiative transition probability of 16,811.81 s⁻¹. The experimental branching ratio for this transition is 0.5925, which is slightly lower than the calculated branching ratio of 0.6149, indicating that there might be some non-radiative transitions occurring in this transition.

On the other hand, the transition from ³P₁ to ³H₅ at a wavelength of 530 nm has a radiative transition probability of 0.00, indicating that this transition is forbidden. The experimental branching ratio for this transition is 0.0743, which is relatively high compared to the calculated branching ratio of 0.0000, indicating that there might be some other processes contributing to the emission at this wavelength.

The transition from ³P₀ to ³H₆ at a wavelength of 616 nm has a radiative transition probability of 1,965.57 s⁻¹. The experimental branching ratio for this transition is 0.1797, which is lower than the calculated branching ratio of 0.0719, indicating that there might be some other transitions contributing to the emission at this wavelength.

Finally, the transition from ³P₀ to ³F₂ at a wavelength of 647 nm has a radiative transition probability of 4,682.11 s⁻¹. The experimental branching ratio for this transition is 0.1534, which is close to the calculated branching ratio of 0.1713, indicating that this transition is mostly radiative. Overall, these findings provide valuable information about the radiative and non-radiative processes occurring in the Pr³⁺ ion-doped glass, which can be useful for the development of new optical and sensing devices.

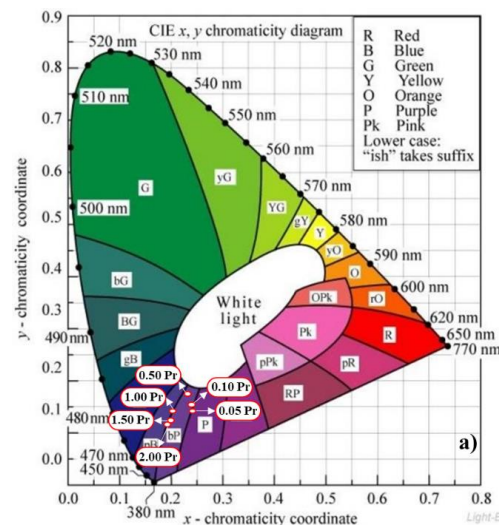
CIE 1931 chromaticity

The CIE coordinates x and y are used to represent the color of a emission, where x and y values between 0 and 1 correspond to the chromaticity diagram. The chromaticity diagram is a 2D representation of all visible colors, and it is commonly used to compare and describe colors. The CIE coordinates of 0.05 Pr³⁺ glass, $x = 0.2320$ and $y = 0.1464$, indicate that the glass has a blue purple as show in Figure 4. The values of x and y can be used to calculate other colorimetric parameters such as color temperature, dominant wavelength, and color purity. The CIE coordinates

are useful for understanding the color properties of the glass and can be used to compare the color of this glass to other materials.

Conclusions

This study investigated the effect of praseodymium (Pr³⁺) ion concentration on the optical and luminescence properties of tellurite glasses. The density of the glasses did not show any trend with the increasing concentration of Pr³⁺, while the molar volume showed a linear trend. The Judd-Ofelt theory was used to calculate the radiative transition probability, stimulated emission cross-section, and branching ratio of the glasses, which were compared to reported values. The estimated J-O intensity characteristics for the Pr³⁺ 0.50 mol% glass are $\Omega_2 = 1.57 \times 10^{-20}$ cm², $\Omega_4 = 4.13 \times 10^{-20}$ cm², and $\Omega_6 = 2.27 \times 10^{-20}$ cm², following the pattern $\Omega_4 > \Omega_6 > \Omega_2$. The CIE coordinates of the glasses were also determined, with the 0.05 mol% Pr³⁺ glass showing a blue purple. These findings support the potential use of these glasses in laser and other optical device applications, particularly for their high radiative transition probabilities and stimulated emission cross-sections.

**Figure 4. The CIE diagram (a) $\lambda_{ex} = 447$ nm of Pr³⁺-doped BaO-ZnF₂ tellurite glasses**

Acknowledgements

N. Sangwaranatee would like to thanks Suan Sunandha Rajabhat University for supporting this research. Authors would like to thank National Research Council of Thailand (NRCT) and Thailand Science Research and Innovation (TSRI) for supporting this research.

Reference

- Aziz, S., Shaharuddin, R., Talib, Z., Mohamed Kamari, H., and Daud, W. (2009). Synthesis and optical properties of ZnO-TeO₂ glass system. *American Journal of Applied Sciences*, 6(8):1489-1494. <https://doi.org/10.3844/ajassp.2009.1489.1494>
- Goldner, P. and Auzel, F. (1996). Application of standard and modified Judd-Ofelt theories to a praseodymium-doped fluorozirconate glass. *Journal of Applied Physics*, 79(10):7972-7977. <https://doi.org/10.1063/1.362347>
- Neethish, M.M., Acharyya, J.N., Prakash, G.V., and Ravi Kanth Kumar, V.V. (2021). Effect of Zinc Fluoride addition on structure of barium Borate glasses for nonlinear optical applications. *Optical Materials (Amst)*, 121:111626. <https://doi.org/10.1016/j.optmat.2021.111626>
- Rai, V.K. and Mohanty, D.K. (2012). Visible upconversion emissions in Pr³⁺-doped TeO₂-ZnO glass. *Applied Physics B*, 109:599-603. <https://doi.org/10.1007/s00340-012-5185-4>
- Rajaramakrishna, R., Wongdeeying, C., Yasaka, P., Limkitjaroenporn, P., Sangwaranatee, N., and Kaewkhao, J. (2019). Pr³⁺ doped BaO:ZnO:B₂O₃: TeO₂ glasses for laser host matrix. *Journal of Metals, Materials and Minerals*, 28(2):47-54.
- Rao, B.R.V., Srinivas Prasad, M.V.V.K., Tanuj Kumar, L., and Venkateswarlu, M. (2018). Spectroscopic investigations on Pr³⁺ doped alkali fluoroborophosphate glasses. *Journal of Nanoscience and Technology*, 04(2):360-363. <https://doi.org/10.30799/jnst.sp202.18040207>
- Shaharuddin, R., Aziz, S., Talib, Z., and Hussein, M. (2008). Effect of Zinc on the Physical Properties of Tellurite Glass. *Journal of Applied Sciences*, 8(10):1956-1961. <https://doi.org/10.3923/jas.2008.1956.1961>
- Tagiara, N.S., Palles, D., Simandiras, E.D., Psycharis, V., Kyritsis, A., and Kamitsos, E.I. (2017). Synthesis, thermal and structural properties of pure TeO₂ glass and zinc-tellurite glasses. *Journal of Non-Crystalline Solids*, 457:116-125. <https://doi.org/10.1016/j.jnoncrysol.2016.11.033>
- Yasaka, P., Boonin, K., Duangjai, K., Kim, H.J., Kothan, S., and Kaewkhao, J. (2022). Luminescence, spectroscopic properties and reddish-orange emission from Eu³⁺ ion doped tellurite and fluorotellurite glasses: A comparative study. *Optik (Stuttg)*, 265:169531. <https://doi.org/10.1016/j.ijleo.2022.169531>
- Yasaka, P., Boonin, K., Kaewkhao, J., Rajaramakrishna, R., and Kothan, S. (2023). Effect of Erbium Oxide on Luminescence and Spectroscopy properties of a zinc barium boro-tellurite glass system for photonic applications. *Physica Status Solidi (A) Applications and Materials Science*, 220(10):2200438. <https://doi.org/10.1002/pssa.202200438>