INFLUENCE OF Dy³⁺ IN PHYSICAL AND OPTICAL BEHAVIOR OF CALCIUM SULFATE ULTRA-PHOSPHATE GLASSES

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ABSTRACT

To examine the influence of trivalent dysprosium ion (Dy³⁺) on physical and optical properties prepared by melt quenching method. The samples composition of 20CaSO₄ (80 - x) P₂O₅ – xDy₂O₃, where x = 0.1, 0.2, 0.3, 0.4 and 0.5mol% were prepared and analyzed. Materials were characterized by X-ray diffraction, UV visible and photoluminescence spectroscopy, amorphous nature of the samples was confirmed by X-ray diffraction technique, UV-Vis for optical measurement and luminescence for excited state dynamics. The UV absorption spectra of the glass sample correspond to ⁶H₁₁/₂ (1673 nm), ⁶H₉/₂ (1262 nm), ⁶F₉/₂ (1087 nm), ⁶H₅/₂ (899 nm), ⁶F₅/₂ (796 nm), ⁶F₃/₂ (753 nm), ⁵G₁₁/₂ (422), ⁴I₁₃/₂ (384) and ⁶P₇/₂ (347). The physical properties comprise of glass density, molar average molar volume, ion concentration, dielectric constant and molar refractive index was determined. The band gap (EₚₑIndexPath), Urbach energies (AE) and refractive index lie in range and decreases with increase in Dy³⁺ concentration. Therefore, Dy³⁺ compositional changes were examined and indicate that dysprosium phosphor could serves as a potential candidate for optical application as laser is included.

Keywords: phosphate, dysprosium ion, melts quench method, absorption spectra, luminescence.

1. INTRODUCTION

Many years back, research on rare earth ions -doped glasses are important for optical devices of distinctive properties identified in color displays and laser materials [1] optical fiber communication [2, 3] light-emitting materials [4] as well as IR to visible converters [5]. In achieving the aims and development on optical materials that are suitable for the above mention application which required a detail performance of optical absorption and the luminescence properties that are solidly depend on the nature as well as the type of local environment in the vicinity of RE ions and the phonon energy of the glass former. The ions (REI) -doped glass systems considered as valuable luminescent materials for solid state lasers within the spectral region (visible and near IR). Dysprosium is one of most fundamental rare earth materials -doped phosphate glasses that attract more attention especially for laser when compare with other ions. For optical amplifier and lasers materials, phosphate, fluoro-borate and bismuth-borate glasses are of great importance [6]. Considering the transitions in dysprosium ions, most well known hypersensitive transitions in Dy³⁺ at ⁴F₉/₂→⁴H₃/₂ are strongly dependant on the nature of the host, but the sensitivity of magnetic dipole’s intensity at ⁴F₉/₂→⁴H₅/₂ transition is less to the host. Therefore, a doped trivalent dysprosium will generate white light at a suitable environment [7]. Furthermore, Phosphate based glasses to a certain extent possess greater thermal expansion coefficients [8,9] and low processing temperatures used as glass sealant, with some interesting optical properties for optical waveguides [9] as biomaterials and also for immobilization of radioactive wastes. Ultra-, Ortho- and Pyrophosphate preparation on calcium phosphate glasses (CaO/P₂O₅ ≥ 2 molar ratio) were achieved using higher percentage of other oxides to modify the phosphate structure such as MgO, SiO₂ or NaO [10]. The main intent of this work is to study the influence of dysprosium on physical and optical behavior of calcium sulfate ultra-phosphate glasses with different Dy₂O₃ concentration.

2. EXPERIMENTAL DETAILS

2.1 Glass preparation

20CaSO₄ (80 - x) P₂O₅ – xDy₂O₃ where x = 0.1,0.2, 0.3, 0.4, and 0.5 mol% glasses were prepared by conventional melt method. Reagent grade of calcium sulfate (CaSO₄), Phosphoric acid (H₃PO₄) and Dysprosium oxide (Dy₂O₃) serve as starting materials for 20g batch/melt having 99.98% purity. The samples were mixed and preheated in an alumina crucible at 300 °C for 30 min then melted at 1200 °C for 1h where the oxygen was bubbled and eliminated. Subsequent annealing at appropriate temperature for 300 °C 5 hrs to release the mechanical and thermal stresses, the melt were then allowed to cool down to room temperature. After which the sample were finely polished and grinded to certain dimension for further characterization then stored in a desiccators prior to assessment.

2.2 XRD measurement

The samples were carefully examined by means of XRD pattern obtained by Siemens Diffractometer (XRD-D5000) of wavelength (Cu Kα, λ= 1.54056 Å) radiation source without having any diffraction lines this verify the glass formation as an amorphous materials processing of broad humps (halo in XRD pattern) at 20 degree range 10-90°.

2.3. UV-Vis measurement

Optical absorption spectra of polished glass samples were determine in the range of 500-1800 nm (wavelength range) using a double beam spectrophotometer as in Figures 3 (a) and (b) with clear
absorption peaks (Using Shimadzu UV-VIS-NIR spectrophotometer).

2.4 Density measurement
In the physical properties, the density result was determine at room temperature using Archimedes process where toluene serves as an immersed liquid of density 0.865 gm/cm³ [11]. The glass weighed in air as \( G_{\text{air}} \) and reweighed in toluene as \( G_{\text{tol}} \) where the density of the glass is given by:

\[
\rho = \frac{G_{\text{air}}}{(G_{\text{air}} - G_{\text{tol}})} * 0.865 \text{ g/cm}^3
\]

(1)

The calculated molar volume \( (V_m) \) was observed using the relation,

\[
V_m = \frac{M}{\rho}, \quad M_T = X_{\text{CaSO}_4}Z_{\text{CaSO}_4^+} + X_{\text{P}_2\text{O}_5}Z_{\text{P}_2\text{O}_5^+} + X_{\text{Dy}_2\text{O}_3}Z_{\text{Dy}_2\text{O}_3} \]

\( \text{XP}_2\text{O}_5 \text{ and XDy}_2\text{O}_3 \) are the mole fraction of all oxides and \( Z_{\text{CaSO}_4} \), \( Z_{\text{P}_2\text{O}_5} \) and \( Z_{\text{Dy}_2\text{O}_3} \) are the molar weight of the oxides.

The density \( (\rho) \) and molar volume \( (V_m) \) dependence as indicated in Figure-1 where the values of density increases linearly with consistent increased in mole percent of dopant and corresponding decreased in molar volume. The increase in density with increase in dysprosium ion content is related to the high molecular mass of dysprosium ions which leads to an expected result, change in molar volume also depend on the rate of change of density \( (\rho) \) and molar weight. Since the molar volume increases with change in dysprosium ion content this account for an increased in the number of NBOs [12]. In determining the refractive index of the samples obtained by using the Dimitrov and Sakka's relation in Table-1 equation (vi).

3. RESULT AND DISCUSSIONS

From Figure-2, shows the X-ray measurement of calcium sulfate ultra-phosphate doped dysprosium oxide, the results obtained verify the amorphous nature of materials as peaks are absence.

3.1. UV-Vis-NIR analysis
The absorption spectra of the sample \( (\text{Dy}^{3+}) \) doped 0.1CSP to 0.5CSP were measured and recorded at normal room temperature as presented in Figures 3 (a) and (b). The spectra comprise of six transitions as the prominent absorption spectra originating from \( ^4\text{H}_{15/2} \) as ground state corresponding to \( \text{Dy}^{3+} \)-doped glasses within NIR region and three transitions in UV-Vis region [9, 10] all energy absorbed lies within UV-Vis-NIR region as previously investigated [13] meanwhile, there is low intensities in the UV-Vis region caused by a spin forbidden transition, all the absorption band were allotted at 347, 384, 422, 753, 796, 899, 1087, 1262 and 1673nm of origin \( ^4\text{H}_{15/2} \text{ Dy}^{3+} \) ground state. The absorption band apportioning to \( ^4\text{I}_{15/2}, ^4\text{H}_{9/2}, ^6\text{F}_{9/2}, ^6\text{F}_{7/2}, ^4\text{F}_{5/2}, ^4\text{F}_{3/2}, ^4\text{G}_{11/2}, ^4\text{I}_{11/2}, ^4\text{I}_{13/2} \) and \( ^4\text{P}_{1/2} \) as reported work [14, 15], the idea of transition correspond to carnell et al [16] as presented in Table-2. Intensities observed were change with dopant \( \text{(Dy}^{3+}) \) concentration where \( ^4\text{F}_{9/2} \text{ and } ^4\text{H}_{9/2} \) act as the hypersensitive transition that follows the selection rule \( |\Delta S| = 0, |\Delta L| \leq 2 \text{ and } |\Delta J| \leq 2 \) [17].
Figure 3. Optical absorption spectra of $20\text{CaSO}_4 (80 - x) \text{P}_2\text{O}_5 – x\text{Dy}_2\text{O}_3$ glasses for (a) UV-Vis and (b) NIR regions.

The excitation spectra of CSP doped with different amount of dysprosium ion (Figure 4) in a range of 300 - 550 nm fluorescence at 577 nm having different excitation band centered at $^4\text{I}_{15/2} \rightarrow ^4\text{F}_{9/2}$ (472 nm), $^6\text{I}_{13/2} \rightarrow ^4\text{F}_{5/2}$ (449 nm), $^4\text{I}_{15/2} \rightarrow ^2\text{G}_{11/2}$ (423 nm), $^6\text{I}_{13/2} \rightarrow ^2\text{I}_{13/2}$ (385 nm), $^4\text{I}_{15/2} \rightarrow ^2\text{P}_{7/2}$ (347 nm) and $^6\text{I}_{13/2} \rightarrow ^2\text{P}_{5/2}$ (323 nm) [17, 18], evidently, the wavelength of larger excitation band gives most intense emission at 347 nm. After excitation at 350 nm, non-radiative relaxation for trivalent dysprosium ions occurred to next lower level of $^4\text{F}_{9/2}$ and emits intense light as indicated in Figure 5, this figure, displays the luminescence spectra of calcium sulfate ultra-phosphate glass doped dysprosium oxide in the region of 450-675 nm at excitation wavelength of 350 nm room temperature. The spectra display three emission peaks at 481, 572, 661 nm ascribed to blue ($^4\text{I}_{15/2} \rightarrow ^4\text{F}_{9/2}$), yellow ($^4\text{I}_{15/2} \rightarrow ^2\text{H}_{13/2}$) and weak red ($^4\text{I}_{15/2} \rightarrow ^2\text{H}_{11/2}$) having less intense when compare with the 2 previous ones as reported [19, 20]. These mechanisms of luminescence process with the excitation wavelength are explained in energy level scheme (Figure 6) of dysprosium ions in calcium sulfate ultra-phosphate glass to define the various color emission (Blue, Yellow and red) originating from $^4\text{I}_{15/2}$ to the ground state of $^4\text{I}_{15/2}$ for J= 15/2, 13/2 and 11/2. GSA for ground state absorption occurred from lower level to the higher energy level (excited energy level). Non-radiative transitions also occurred due to vibrational relaxation between excited energy level that results in internal conversion and return back to ground state thereby emitting different colors of blue, yellow and red [21-23].
The absorption mechanism of dopant such as optical band gaps (Tauc’s gap) for direct and indirect, Urbach’s energy, and other parameters as evaluated in Table-2 and described by equation (xi) Table-1 as n stands for the fraction of 3, 2, 1/2, and 3/2 for allowed indirect, forbidden direct, allowed direct, and forbidden indirect transitions [24, 25] but it all depends on the nature of electron transitions. It is observed that for many amorphous materials the values obtained qualify n = 2 for direct (Figure-6) and n = 1/2 for indirect (Figure-7), where the optical bang gap (direct) were obtained by plotting the values of \((\alpha \nu h)^2 [eV \cdot cm^{-1}]^2\) against \(\nu h (eV)\) and indirect mechanism \((\alpha \nu h)^{1/2}[eV \cdot cm^{-1}]^{1/2}\) against \(\nu h (eV)\), band gap energy serve as energy difference between the two level of valance band and conduction band [26]. Preferably, in amorphous materials the optical transition should be indirect due to lack of translation symmetry as a result of undefined wave vector [27]. The direct optical band gap decreases with increase in dysprosium ions contents this leads to the changes in the structure of glass network and also there is decrease in band gap [7, 28]. Meanwhile, in many solid materials, glass is part of the materials that transmit light within a visible region, therefore, studying the refractive index of the sample are considered important, its serves as the fundamental parameter related to optical devices performance and reliability.

The increase in Dy\(^{3+}\) ions (Table-2) may causes structural changes and enhances the rate of electron localization thereby establishing the defect in the charge distribution [29], as observed that the changes in donor center when adding dopant leads to the decreased in bang gap energy [30, 31].

This energy (Urbach) in Figure-8 is the amount of disorderliness in amorphous materials; higher urbach energy \((\Delta E)\) values indicate that the materials are glassier in nature [29]. All values of the energies obtain are found to be in ranges with corresponding change in dysprosium ions as enlisted in Table-2.

![Figure-6. Energy level diagram for CSP: Dy glasses.](image)

![Figure-7. Direct band gap for CSP:Dy glasses.](image)
Table-1. Equation used for physical parameters.

<table>
<thead>
<tr>
<th>Eg.</th>
<th>Measurement</th>
<th>Formula</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i)</td>
<td>Density (ρ)</td>
<td>( \rho = \frac{G_{\text{air}} - G_{\text{tol}}}{\rho_{\text{air}}} \times 0.865 \text{g/cm}^3 )</td>
<td>( \rho ) is density, ( G_{\text{air}} ) is the weight of glass in air, ( G_{\text{tol}} ) is the weight of glass in toluene.</td>
</tr>
<tr>
<td>(ii)</td>
<td>Molar volume, (Vm)</td>
<td>( V_m = \frac{M_T}{\rho} )</td>
<td>( V_m ) is the molar volume, ( M_T ) is the total molecular weight.</td>
</tr>
<tr>
<td>(iii)</td>
<td>Ion concentration, (N)</td>
<td>( N = \frac{x(N_A)}{M_T} )</td>
<td>( x ) is the mole fraction of RE oxide, ( N_A ) is the Avogadro's number.</td>
</tr>
<tr>
<td>(iv)</td>
<td>Polarizability, ( r_p ) (Å)</td>
<td>( r_p (\text{Å}) = \left( \frac{1}{N} \right)^{1/3} )</td>
<td>( r_p ) is the Polaron radius.</td>
</tr>
<tr>
<td>(v)</td>
<td>Inter-nuclear distance, ( r_i ) (Å)</td>
<td>( r_i (\text{Å}) = \left( \frac{1}{N} \right)^{1/3} )</td>
<td>( r_i ) is the inter-nuclear distance.</td>
</tr>
<tr>
<td>(vi)</td>
<td>Refractive index, n</td>
<td>( n = \left( \frac{n^2 - 1}{n^2 + 2} \right)^{1/2} \left( \frac{E_g}{20} \right) )</td>
<td>( E_g ) is the energy band gap, ( n ) is the refractive index.</td>
</tr>
<tr>
<td>(vii)</td>
<td>Reflection loss (R)</td>
<td>( R = \left( \frac{n + 1}{n - 1} \right)^2 )</td>
<td>R is the reflection loss.</td>
</tr>
<tr>
<td>(viii)</td>
<td>Dielectric constant (ε)</td>
<td>( \varepsilon = n^2 )</td>
<td>( \varepsilon ) is dielectric constant.</td>
</tr>
<tr>
<td>(ix)</td>
<td>Field strength (F)</td>
<td>( F = \frac{Z}{r_p^2} )</td>
<td>( Z ) is the atomic number of RE ions.</td>
</tr>
<tr>
<td>(x)</td>
<td>Molar refractivity (Rm)</td>
<td>( R_m = \left( \frac{n^2 - 1}{n^2 + 2} \right)^{1/2} )</td>
<td>( R_m ) is the molar refraction.</td>
</tr>
<tr>
<td>(xi)</td>
<td>Absorption coefficient, ( \alpha )</td>
<td>( \alpha = \frac{nhv}{A(E_g - h\nu)} )</td>
<td>( \alpha ) is the absorption coefficient, ( h\nu ) is the photon energy, ( A ) is constant ( n ) for direct and indirect transition.</td>
</tr>
</tbody>
</table>

Table-2. Physical parameters of (20CaSO4 (80 – x) P2O5 – xDy2O3 glasses.

<table>
<thead>
<tr>
<th>Physical measurements</th>
<th>Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>x mol % of Dy2O3</td>
<td>0.1</td>
</tr>
<tr>
<td>Av. molar weight (g/mole)</td>
<td>103.299</td>
</tr>
<tr>
<td>Density ( \rho ) (g/cm³)</td>
<td>2.145</td>
</tr>
<tr>
<td>Molar volume, ( V_m ) (cm³)</td>
<td>48.157</td>
</tr>
<tr>
<td>Ion concentration ( (N \times 10^{21}) )</td>
<td>3.270</td>
</tr>
<tr>
<td>Polarizability, ( r_p ) (Å) ( \times 10^{-8} )</td>
<td>2.715</td>
</tr>
<tr>
<td>Inter-nuclear distance, ( r_i ) (Å) ( \times 10^{-8} )</td>
<td>6.737</td>
</tr>
<tr>
<td>Field strength, ( F \times 10^{17} ) (cm²)</td>
<td>0.895</td>
</tr>
<tr>
<td>Refractive index</td>
<td>2.138</td>
</tr>
<tr>
<td>Reflection loss</td>
<td>0.1315</td>
</tr>
<tr>
<td>Dielectric constant, ( \varepsilon )</td>
<td>4.571</td>
</tr>
<tr>
<td>Direct band gap (eV)</td>
<td>4.169</td>
</tr>
<tr>
<td>Indirect band gap (eV)</td>
<td>4.209</td>
</tr>
<tr>
<td>Urbach energy ( \Delta E ) (eV)</td>
<td>0.250</td>
</tr>
</tbody>
</table>
4. CONCLUSIONS

Dysprosium oxide (Dy\textsuperscript{3+}) doped calcium sulfo-phosphate was properly prepared and achieved using conventional melt quench method and verified the structure by XRD pattern. Therefore, the influence of Dy\textsuperscript{3+} on physical and optical properties was investigated. In physical properties, it indicates that the density and refractive index increases while molar volume decreases with increase in Dy\textsuperscript{3+} ion concentration. The optical values for direct and indirect transitions observed by Tauc's plot are obviously depending on composition that is sensitive to dopant (Dy\textsuperscript{3+}). Larger bang gap range from 4.087 - 4.169 eV indicate that the glass is fit for optical applications, since most glasses with visible luminescence in yellow (Dysprosium), orange (Samarium) have potential application in opto-electronic and displays.

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