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Study of the physical and optical properties of Holmium Ion doped soda lime silicate glasses

การศึกษาสมบัติทางกายภาพและทางแสงของแก้วโซดาไลม์ซิลิเกตที่เติมไอออนของโฮลเมียม

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Abstract

The aim of this present work is to investigate the physical and optical properties of Ho_2O_3 doped soda lime silicate glasses. Soda lime silicate (SLS) glasses with the compositions of (65-x)SiO_2 : 25Na_2O : 10CaO : xHo_2O_3 (where x = 0.0, 0.5, 1.0, 1.5, 2.0 and 2.5 mol%) were prepared by melt-quenching technique and characterized their properties by using density, refractive index and optical absorption. The obtained density (ρ), molar volume (V_M) and refractive index (n_D) were found to increase with increase in the concentration of Ho_2O_3 in the glass matrix. Such behavior was accredited to the differences between atomic weight and the atomic radii of the Si^{4+} and Ho^{3+} ions. The rare earth ion concentration (N) and ionic radius (r_p) were calculated. The absorption spectra of Ho^{3+} exhibit eight transitions from the $^5I_8$ ground state to the various excited states such as to $^3H_6$ (361 nm), $^5G_4$ (386 nm), $^5G_5$ (418 nm), $^5G_6$ (454 nm), $^5F_3$ (487 nm), $^5S_2$ ($^5F_4$) (537 nm), $^5F_5$ (640 nm) and $^5I_6$ (1151 nm) of the Ho^{3+} ions.

Keywords: density, refractive index, molar volume, absorption, glasses

บทคัดย่อ

งานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาสมบัติทางกายภาพและทางแสงของระบบแก้วโซดาไลม์ซิลิเกตที่เติมโฮลเมียมออกไซด์ ตัวอย่างแก้วถูกเตรียมขึ้นในห้องปฏิบัติการด้วยเทคนิค meting quenching โดยมีสูตรเคมี คือ (65-x)SiO_2 : 25Na_2O : 10CaO : xHo_2O_3 (เมื่อ x คือปริมาณความเข้มข้นของโฮลเมียมออกไซด์ มีค่าตั้งแต่ 0.0, 0.5, 1.0, 1.5, 2.0 และ 2.5 mol%) ผลการศึกษาพบว่าค่าความหนาแน่น ปริมาตรเชิงโมล และดัชนีหักเหของตัวอย่างแก้วจะมีค่าเพิ่มขึ้นตามปริมาณความเข้มข้นของโฮลเมียมออกไซด์ เนื่องจากมวลอะตอมและรัศมีอะตอมของ Si^{4+} และ Ho^{3+} มีค่าแตกต่างกัน สำหรับสเปกตรัมการดูดกลืนแสงของตัวอย่างแก้ว พบพีคการดูดกลืนเกิดขึ้นที่ความยาวคลื่น 361 nm, 386 nm, 418 nm, 454 nm, 487 nm, 537 nm, 640 nm และ 1151 nm ซึ่งเกิดขึ้นจากการเปลี่ยนระดับพลังงานของ Ho^{3+} ไอออน จากสถานะพื้น $^5I_8$ ไปยังสถานะกระตุ้น $^3H_6$, $^5G_4$, $^5G_5$, $^5G_6$, $^5F_3$, $^5S_2$ ($^5F_4$), $^5F_5$ และ $^5I_6$ ตามลำดับ

คำสำคัญ: ความหนาแน่น, ดัชนีหักเห, ปริมาตรเชิงโมล, การดูดกลืน, แก้ว

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1. Introduction

Glasses doped with rare earth ions are of great significance because these glasses have found many applications in devices such as solid state lasers, up converters and optical fibers. Ho^{3+} is one of the most attractive candidates for dopant among the RE ions. It shows strong luminescence at various wavelengths including the visible region [1] and has been widely studied due to laser action at infrared and visible regions. Infrared laser emissions of Ho^{3+} ion in the range of 1.2–4.9 μm have been proven, and some infrared emissions are in the transmission window region where the optical loss of fiber remains low [2]. Visible laser emissions of Ho^{3+} ion can be acquired by the up conversion processes. The up conversion luminescence of lanthanide ions doped several glass materials have been fascinating as optical devices such as optical amplifiers, optical data storage, color display, under-sea optical communications, biomedical diagnostics and sensors, etc. [2]. Among the rare earth ions, Ho^{3+} ion is also one of the most important active ions applied to up conversion luminescence, because of its favorable energy level structure. For example, the Ho^{3+} ion has a relatively long-lasting $^5I_7$ level which can act as a good population reservoir for possible up conversion processes with a large peak stimulated emission cross-sections [3]. Additionally, the Ho^{3+} ion make available eye-safe potential laser emission even at room temperature (RT) with a low threshold action that has appealing applications in atmospheric communication systems [4]. Also, the $^5S_2$ ($^5F4$) $\longrightarrow {}^5I_8$ transition of Ho^{3+} ion is a hypersensitive transition therefore it reliant on host. So, it is expected that glasses doped with Ho^{3+} ion are the important candidates for both ~547 nm ($^5S_2$ ($^5F4$) $\longrightarrow {}^5I_8$) and ~2 μm ($^5I_7 \longrightarrow {}^5I_8$) emissions which are suitable for the development of visible and IR solid state lasers, respectively [3]. Likewise, continuous wave green up conversion lasing has also been verified in Ho^{3+} ion doped glass fibers pumped with red light [5].

Silicate glasses are outstanding hosts for rare earth ions and most of recent fiber lasers are constructed with silica fibers due to their low loss, high tenability, and strong strength [6]. These glasses are chemically durable, thermally stable and optically transparent at the excitation and lasing wavelength [7]. In this regard the soda lime silicate glass has been found to be an appropriate optical material having high transparency, low melting point, high thermal stability and good rare earth ions solubility. Moreover, in the development of optical devices, these glasses are found to be more compatible with the fabrication process.

2. Objectives

In this present work, the Ho^{3+} doped soda lime silicate glass has been studied for its physical and optical properties, in which Na_2O has been used as a primary modifier and CaO as secondary modifier for decreasing the melt viscosity when high silicate contents are used in glass formation.

3. Experimental studies

The Ho^{3+} doped soda lime silicate glasses were $(65\text{-}x)SiO_2 : 25Na_2O : 10CaO : xHo_2O_3$ with $0 \le x \le 2.5$ (mol%) prepared by the conventional melt quenching technique using appropriate amount of high purity analytical grade chemicals (99.99%) such as SiO_2, Na_2O, CaO and Ho_2O_3. They were thoroughly mixed by hand milling in a high purity alumina crucible for 30 min and then melted at 1500 °C by an electrical muffle furnace for 3 hours in open air. After complete melting, the melts were quickly poured into a preheated stainless steel mold and annealed at 500 °C for 3 hours before being cooled down to room temperature. Finally, the as-prepared glass samples were cut and then fine polished to a dimension of 1.0 cm. × 1.5 cm. × 0.3 cm. The glass code and the chemical compositions are as follows in Table 1.

Table 1 Chemical composition of as-prepared glasses

Glass samples	Ho_2O_3 (mol%)	Glass composition (mol%)
0.0Ho:SLS (Host)	0.00	$65.0Si_2O$-$25.0Na_2O$-10.0CaO
0.5Ho:SLS	0.50	$64.5Si_2O$-$25.0Na_2O$-10.0CaO-$0.5Ho_2O_3$
1.0Ho:SLS	1.00	$64.0Si_2O$-$25.0Na_2O$-10.0CaO-$1.0Ho_2O_3$
1.5Ho:SLS	1.50	$63.5Si_2O$-$25.0Na_2O$-10.0CaO-$1.5Ho_2O_3$
2.0Ho:SLS	2.00	$63.0Si_2O$-$25.0Na_2O$-10.0CaO-$2.0Ho_2O_3$
2.5Ho:SLS	2.50	$62.5Si_2O$-$25.0Na_2O$-10.0CaO-$2.5Ho_2O_3$

Table 2 Some properties of as-prepared glasses

Properties		Glass samples					
		0.0Ho:SLS	0.5Ho:SLS	1.0Ho:SLS	1.5Ho:SLS	2.0Ho:SLS	2.5Ho:SLS
Average molecular weight	M (g)	60.1566	61.7454	63.3343	64.9232	66.5121	68.1009
Thickness	d (cm)	0.3950	0.3800	0.3850	0.3750	0.3250	0.3600
Dielectric constant	ε	2.3241	2.3342	2.3478	2.3630	2.3771	2.3887
Optical dielectric constant	$p\frac{dt}{dp}$	1.3241	1.3342	1.3478	1.3630	1.3771	1.3887
Ho^{3+} ion concentration	N ($\times 10^{20}$ ions/cm)	-	1.2612	2.5111	3.7531	4.9722	6.1794
Inter-ionic distance	R_i ($\mathring{A}$)	-	19.9405	15.8506	13.8634	12.6227	11.7404
Molar refractivity	R_m (cm^{-3})	7.2506	7.3489	7.4343	7.5187	7.6210	7.7090
Refractive loss	R (%)	4.3166	4.3597	4.4181	4.4829	4.5435	4.5929
Molecular electronic polarizibility	α_m ($\times 10^{-26}$ cm^3)	-	5.8243	2.9460	1.9863	1.5099	1.2219

4. Physical and optical studies

4.1 Density and molar volume

The weight of the prepared glass samples was measured in air and in xylene using a 4-digit sensitive microbalance (Denver, Pb214) by applying Archimedes principle. Then, the density (ρ) was calculated by using the relation

$$\rho = \frac{W_a}{W_a - W_b} \times \rho_b \tag{1}$$

where W_a is the weight of glass sample in air, W_b is the weight in xylene and ρ_b is the density of xylene (ρ_b = 0.863 g/cm^3). The corresponding molar volume (V_M) was calculated using the relation,

$$V_M = M_T / \rho_b \tag{2}$$

where M_T is the total molecular weight of the multi-component glass system given by

$$M_T = x_{SiO_2}W_{SiO_2} + x_{Na_2O}W_{Na_2O} + x_{CaO}W_{CaO} + x_{Ho_2O_3}W_{Ho_2O_3} \tag{3}$$

where x_{SiO_2}, x_{Na_2O}, x_{CaO} and $x_{Ho_2O_3}$ are the mole fractions of the constituent oxides, whereas W_{SiO_2}, W_{Na_2O}, W_{CaO} and $W_{Ho_2O_3}$ are the molecular weight of the constituent oxides.

4.2 Refractive index and other properties

Refractive index is another significant property to be measured with respect to the optical features of glass. Therefore, a large number of researchers have carried out studies to determine the relation between refractive index and glass composition. The refractive index of the glasses was measured at 589.3 nm (sodium wavelength) using an Abbe refractometer with monobromo-naphthalene as the contact liquid.

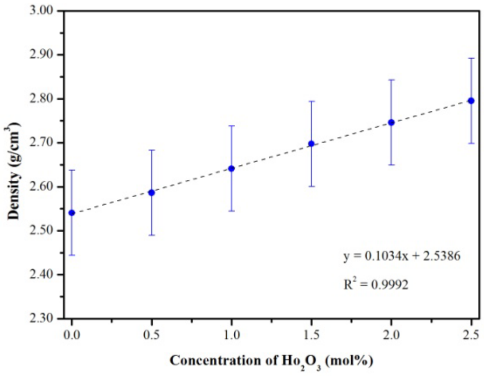

Figure 1 The variation of density with the Ho_2O_3 concentration

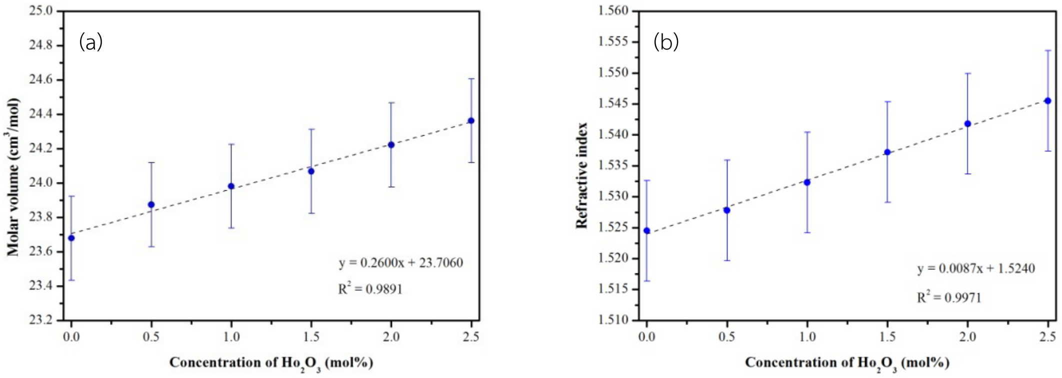

Figure 2 The variation of (a) molar volume and (b) refractive index with Ho_2O_3 concentration

Physical parameters such as, concentration of Ho^{3+} ions, inter-ionic distance, molar polarizibility and reflection losses of the Ho:SLS glasses have been obtained and are presented in Table 2.

5. Results and discussion

5.1 Physical properties

The density is a powerful tool capable of exploring the variations in the structure of glasses. The density is affected by the structural softening/ compactness, change in coordination number, cross-link density and dimension of interstitial spaces of the glass. It is evident from Figure 1, that the density increases with the addition of Ho_2O_3 content into the glass network. This indicates that the substitution of SiO_2 by the addition of small amount of Ho_2O_3 results in the increase of average molecular weight of oxide ions in the glass samples under study. Generally, it is expected that the density and molar volume should display opposite behaviors to each other, but in the glasses under study the behavior is different. The molar volume depends on both the rate of change of density and molecular weight.

The molar volume rises over the dopant concentration as can be seen from Table 2 and Figure 2(a). The gradual increase in molar volume of the glass systems with the increase in Ho_2O_3 concentration at the expense of SiO_2, is accredited to the increase in the number of non-bridging oxygen (NBOs) content resulting in the opened glass network structure [8].

Figure 2(b) shows the variation of the refractive index with Ho_2O_3 content. The refractive index of Ho:SLS glasses increases as the Ho_2O_3 concentration increases. The addition of Ho_2O_3 brought about structural changes in Ho:SLS glasses by changing the extended O-Si-O network forming regular SiO_4 tetrahedra to SiO_3 trignonal pyramids, resulting an increase in the non-bridging oxygen to bridging oxygen ratio.

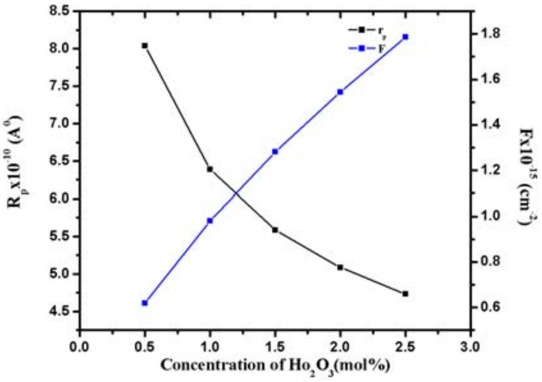

Figure 3 The variation of field strength (*F*) and polaron radius (R_p) with Ho_2O_3 content

The Ho^{3+} ion concentration (N) is calculated using the formula [9]

$$N\,(ions/cm^3) = \frac{(Avogadro's\ \ number)(Glass\ density)}{Average\ molecular\ weight} \times (mol\%\ of\ Ho^{3+}\ ions) \quad (4)$$

It is observed from the Table 2 that the ion concentration increases with increasing Ho_2O_3 content in the glass compositions. It should be mentioned that the Ho^{3+} ions are assumed to be uniformly distributed in the glass matrix. The obtained values of *N* are used to calculate the polaron radius (R_p) and inter nuclear distance (R_i) [10] according to the relations

$$R_p = \frac{1}{2} \times \left(\frac{\pi}{6N}\right)^{1/3} \quad (5)$$

and

$$R_i = \left(\frac{1}{N}\right)^{1/3} \quad (6)$$

where *N* is the number of Ho^{3+} ions per unit volume.

The observed decrease of R_p with increasing Ho_2O_3 content is most likely related to the increased value of (*N*) for Ho^{3+} ions. The RE ions are positioned between the layers and therefore the average RE-oxygen distance decrease. Consequently, the Ho-O bond strength increase, generating a stronger field around the Ho^{3+} ions. The field strength (*F*) around Ho^{3+} ions is calculated according to the formula [8].

$$F\ (cm^{-2}) = \left(\frac{Z}{R_p^2}\right) \quad (7)$$

where *Z* is the atomic number of the Ho^{3+} ion.

Figure 3 shows the variation of *F*, and R_p over the dopant concentration. The obtained values *N*, *and* R_i are also listed in Table 2.

5.2 Optical properties

The absorption spectra of the as-prepared Ho_2O_3 doped glasses were recorded in the UV–Vis–NIR region in the range of 200-1800 nm and shown in Figure 4. As evident from this figure, the undoped glass exhibited no absorption and peaks appeared only with the doping of Ho_2O_3 from 0.5 to 2.5 mol%. Various transitions are observed in the absorption spectra of the glass under study, corresponding to different energy states. The absorption spectra exhibit eight transitions from the $^5I_8$ ground state to the various excited states such as to $^3H_6$ (361 nm), $^5G_4$ (386 nm), $^5G_5$ (418 nm), $^5G_6$ (454 nm), $^5F_3$ (487 nm), $^5S_2$ ($^5F_4$) (537 nm), $^5F_5$ (640 nm) and $^5I_6$ (1151 nm) of the Ho^{3+} ions. The observed transitions are similar to the reported literature [3]. Moreover, the intensity of the absorption peaks increased with the increase in dopant concentration. Among these transitions, $^5I_8 \rightarrow {}^5G_6$ transition is hypersensitive in nature and governed by the selection rules $\Delta S = 0$, $\Delta L \leq 2$ and $\Delta J \leq 2$ [11].

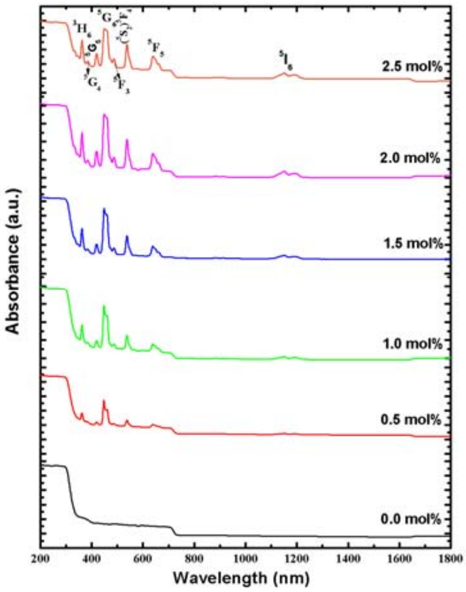

Figure 4 Optical spectra of soda lime silicate glass doped with Ho_2O_3

From the Figure 4, the intensity of hypersensitive transition display a maximum for 2.5 mol% and a minimum for glass sample containing 0.5 mol% Ho_2O_3. This shows that the non-symmetric component of electric field acting on Ho^{3+} ion is low for glass containing 0.5 mol% and high for 2.5 mol% of Ho_2O_3. It might be due to the formation of NBO's around 2.5 mol% concentration of Ho_2O_3. The formation of non-bridging oxygen from bridging oxygen intensifies the symmetry of the bond to the adjacent network cations. The weak $^6H_{15/2} \rightarrow {}^4I_{15/2}$ transition has a magnetic dipole nature [12] while other are electric dipole in nature.

6. Conclusion

The influence of Holmium oxide ions on some physical and optical properties of soda lime silicate glasses has been investigated at various dopant concentrations. The density and refractive index increase with an increase in concentration of Ho_2O_3. The increase in molar volume with Ho_2O_3 contents indicates the extension of glass network due to increase in the number of NBOs. The absorption spectra consist of absorption bands corresponding to the absorption from the ground state $^5I_8$ to $^3H_6$ (361 nm), $^5G_4$ (386 nm), $^5G_5$ (418 nm), $^5G_6$ (454 nm), $^5F_3$ (487 nm), $^5S_2$ ($^5F_4$) (537 nm), $^5F_5$ (640 nm) and $^5I_6$ (1151 nm) of the Ho^{3+} ions. The optical absorption results are indicating a higher covalency of the Ho-O bond for glass containing 2.5 mol% of Ho_2O_3. In addition, a lowest covalency is observed in glass with 0.5 mol% Ho_2O_3.

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