

HOLMIUM IONS-ACTIVATED ZINC-SULFO-BORO-PHOSPHATE  
NANOCOMPOSITES WITH SILVER NANOPARTICLES SENSITIZATION

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UNIVERSITI TEKNOLOGI MALAYSIA

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## ABSTRACT

Rare-earth ions (REIs)-doped oxide glasses and glass-ceramics (GCs) became promising for various photonic applications. However, the inherent small emission cross-section of the REIs-doped systems for practical applications need substantial enhancement. Despite some studies on holmium ion ( $\text{Ho}^{3+}$ ) luminescence from different hosts, the radiative properties of  $\text{Ho}^{3+}$  in zinc-sulfo-boro-phosphate GCs for the miniaturized and inexpensive lasers development remains deficient. In addition, the lasing potency of  $\text{Ho}^{3+}$ -doped phosphate-based GC nanocomposites (GCNCs) with silver nanoparticles (Ag NPs) sensitization has not widely been explored. Thus, the structural, microstructural, impedance, optical and radiative properties of some Ag NPs and  $\text{Ho}^{3+}$  co-doped zinc-sulfo-boro-phosphate GCNCs were evaluated. Three series of samples with the composition of  $(40-x)\text{P}_2\text{O}_5-30\text{B}_2\text{O}_3-30\text{ZnSO}_4-x\text{Ho}_2\text{O}_3$ , where  $x = 0.0, 0.2, 0.4, 0.5, 0.6, 0.8$  and  $1.0$  mol%;  $(39.5-y)\text{P}_2\text{O}_5-30\text{B}_2\text{O}_3-30\text{ZnSO}_4-0.5\text{Ho}_2\text{O}_3-y\text{Ag}$  nanopowder, where  $y = 0.6, 0.7, 0.8$  and  $0.9$  mol%; and  $(39.5-z)\text{P}_2\text{O}_5-30\text{B}_2\text{O}_3-30\text{ZnSO}_4-0.5\text{Ho}_2\text{O}_3-z\text{AgCl}$ , where  $z = 0.6, 0.7, 0.8$  and  $0.9$  mol% were prepared using melt-quenching method. Structural characteristics of the samples were determined using X-ray diffraction (XRD), Fourier transform infrared (FTIR), Raman, energy dispersive X-ray (EDX), X-ray photoelectron spectroscopy (XPS) and density measurements. Microstructures of the samples were analyzed using high-resolution transmission electron microscope (HRTEM) and impedance spectroscopy (IS). Optical properties of the samples were measured using ultraviolet-visible-near infrared (UV-Vis-NIR) and photoluminescence (PL) spectroscopy. The XRD analyses of the as-quenched samples verified their GC nature. The observed increase and decrease in the samples density was attributed to the formation of more bridging oxygen (BO) and non-bridging oxygen (NBO), respectively. The density results of these GCs and GCNCs were supported by the FTIR, Raman and XPS spectral data analyses. The HRTEM images reconfirmed the GC nature of the samples and the existence of the Ag NPs within the network structure. The optical energy band gap, refractive index and Urbach energy were calculated from the UV absorption spectra to get the information about the local structural surroundings. The GC doped with 0.5 mol% of  $\text{Ho}_2\text{O}_3$  exhibited the highest intensity of the red and green PL emissions. Furthermore, the GCNC doped with 0.8 mol% of Ag NPs (mean diameter of 20 nm) revealed the optimum PL intensity enhancement and strongest LSPR absorption band. The obtained larger values of the fluorescence branching ratio and emission cross-section compared to the existing state-of-the-art reports indicated the benefits of the studied samples for the construction of green and red wavelength lasers. A correlation between structural and optical properties was also established for the first time. The studied Ag NPs and  $\text{Ho}^{3+}$  co-doped phosphate-based GCNCs were asserted to be potential for the efficient photonic devices advancement. It is concluded that via the systematic composition optimization, these new types of GCNCs with customized lasing potency can be achieved.

## ABSTRAK

Kaca oksida dan kaca seramik (GC) terdop ion nadir bumi (REI) menjadi sangat berpotensi untuk pelbagai aplikasi fotonik. Walau bagaimanapun, keratan rentas pancaran yang kecil dalam sistem terdop-REI untuk kegunaan praktikal memerlukan peningkatan yang besar. Walaupun terdapat beberapa kajian mengenai pendarcahayaan ion holmium ( $\text{Ho}^{3+}$ ) daripada hos yang berbeza, kajian terhadap sifat pancaran  $\text{Ho}^{3+}$  dalam sistem GC zink-sulfo-boro-fosfat untuk pembangunan laser bersaiz mini dan murah masih kurang. Tambahan pula, keupayaan untuk laser komposit nano GC berasaskan fosfat terdop  $\text{Ho}^{3+}$  dengan pemekaan zarah nano perak (Ag NP) masih belum diterokai sepenuhnya. Oleh itu, struktur, struktur mikro, impedans, sifat-sifat optik dan pancaran beberapa GCNC zink-sulfo-boro-fosfat ko-dop Ag NP dan  $\text{Ho}^{3+}$  telah dinilai. Tiga siri sampel dengan komposisi kimia  $(40-x)\text{P}_2\text{O}_5-30\text{B}_2\text{O}_3-30\text{ZnSO}_4-x\text{Ho}_2\text{O}_3$  di mana  $x = 0.0, 0.2, 0.4, 0.5, 0.6, 0.8$  dan  $1.0$  mol%,  $(39.5-y)\text{P}_2\text{O}_5-30\text{B}_2\text{O}_3-30\text{ZnSO}_4-0.5\text{Ho}_2\text{O}_3-y\text{Ag}$  serbuk nano di mana  $y = 0.6, 0.7, 0.8$  dan  $0.9$  mol%, dan  $(39.5-z)\text{P}_2\text{O}_5-30\text{B}_2\text{O}_3-30\text{ZnSO}_4-0.5\text{Ho}_2\text{O}_3-z\text{AgCl}$  di mana  $z = 0.6, 0.7, 0.8$  and  $0.9$  mol% telah disediakan dengan menggunakan kaedah lindap-kejut leburan. Ciri-ciri struktur sampel telah ditentukan menggunakan pembelauan sinar-X (XRD), spektroskopi inframerah transformasi Fourier (FTIR), Raman, sinar-X sebaran tenaga (EDX), fotoelektron sinar-X (XPS) dan pengukuran ketumpatan. Struktur mikro sampel telah dianalisa dengan menggunakan mikroskop elektron penghantaran resolusi tinggi (HRTEM) dan spektroskopi impedans (IS). Sifat-sifat optik sampel telah diukur dengan menggunakan spektroskopi ultra ungu-cahaya nampak-inframerah hampir (UV-Vis-NIR) dan kefotopendarcahayaan (PL). Analisis XRD terhadap sampel lindap-kejut yang terhasil mengesahkan sifat semula jadi GC. Peningkatan dan penurunan ketumpatan sampel yang dicerap masing-masing dikaitkan kepada pembentukan lebih banyak oksigen berangkai (BO) dan oksigen tak berangkai (NBO). Keputusan ketumpatan GC dan GCNC ini disokong oleh hasil analisis data spektra FTIR, Raman dan XPS. Imej HRTEM mengesahkan sifat semulajadi GC sampel dan kewujudan Ag NP dalam struktur rangkaian. Jurang jalur tenaga optik, indeks biasan dan tenaga Urbach dikira dari spektra penyerapan UV untuk mendapatkan maklumat mengenai persekitaran struktur setempat. Sampel GC didop dengan  $0.5$  mol%  $\text{Ho}_2\text{O}_3$  menunjukkan keamatan pancaran PL merah dan hijau yang tertinggi. Seterusnya, GCNC didop dengan  $0.8$  mol% Ag NP dengan diameter min  $20$  nm, menunjukkan peningkatan keamatan PL yang optimum dan jalur penyerapan LSPR yang kuat. Nilai nisbah cabang pendarfluor dan keratan rentas pancaran yang diperolehi adalah lebih tinggi berbanding dengan nilai terkini yang telah dilaporkan, menunjukkan keberkesanan sampel yang dikaji untuk pembangunan laser panjang gelombang hijau dan merah. Korelasi antara sifat-sifat struktur dan optik juga telah diperolehi untuk pertama kalinya dalam kajian ini. GCNC berasaskan fosfat ko-dop Ag NP dan  $\text{Ho}^{3+}$  yang dikaji adalah sangat berpotensi untuk kemajuan peranti fotonik yang cekap. Adalah disimpulkan bahawa melalui keadah pengoptimuman komposisi yang sistematik, satu jenis GCNC yang baharu, sesuai dengan keupayaan laser yang dikehendaki boleh dicapai.

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## LIST OF SYMBOLS

$A$	-	Absorbance
$\alpha$	-	Absorption coefficient
$\sigma_{Ac}$	-	AC conductivity
$\text{\AA}$	-	Angstrom
$A_{abs}$	-	Area under the absorption peak
$M_{av}$	-	Average molecular weight
$N_A$	-	Avogadro's number
$B$	-	Boron
$B_2O_3$	-	Boron oxide
$f_{cal}$	-	Calculated oscillator strength
$C$	-	Carbon
$cm$	-	Centimeter
$e$	-	Charge of electron
$\epsilon^*$	-	Complex dielectric constant
$Z^*$	-	Complex impedance
$^{\circ}C$	-	Degree Celsius
$\rho$	-	Density (Archimedes principle)
$D_T$	-	Density (Theoretical)
$\tan\delta$	-	Dielectric loss
$\theta$	-	Diffacted angle of the X-Ray beam
$f_{ed}$	-	Electric dipole oscillator strength
$S_{ed}$	-	Electric dipole transition strength
$J'$	-	Excited state's total angular momentum
$\psi'$	-	Excited state's wave function
$f_{exp}$	-	Experimental oscillator strength
$F$	-	Farad
$F_s$	-	Field strength
$\beta_R$	-	Fluorescence branching ratio
$f$	-	Frequency

g	-	Gram
J	-	Ground state's total angular momentum
$\psi$	-	Ground state's wave function
Hz	-	Hertz
N	-	Ho <sup>3+</sup> concentration per cm <sup>3</sup>
Ho <sub>2</sub> O <sub>3</sub>	-	Holmium oxide
Ho	-	Holmium
Ho <sup>3+</sup>	-	Holmium ion/s
$\epsilon''$	-	Imaginary part of the complex dielectric constant
$\lambda_p$	-	Intensity of the PL peak
$r_i$	-	Inter-nuclear distance
$\Omega_j$	-	J-O parameters and j = 2,4 and 6
T <sub>j</sub>	-	Judd's notation of Intensity parameters and j = 2,4 and 6
k	-	Kilo (10 <sup>3</sup> )
$f_{md}$	-	Magnetic dipole oscillator strength
$S_{md}$	-	Magnetic dipole transition strength
m <sub>e</sub>	-	Mass of electron
U <sub>j</sub>	-	Matrix elements and j = 2,4 and 6
M	-	Mega (10 <sup>6</sup> )
m	-	Meter
$\mu$	-	Micro
$\epsilon(\nu)$	-	Molar extinction coefficient
$\alpha_m$	-	Molar polarizability
$R_m$	-	Molar refractivity
V <sub>m</sub>	-	Molar volume
x	-	Mole fraction of the component in the composition
n	-	Nano (10 <sup>-9</sup> )
q	-	Number of transitions in the oscillator strength fitting
$\Omega$	-	Ohm
E <sub>g</sub>	-	Optical band gap energy
O	-	Oxygen
H <sub>3</sub> PO <sub>4</sub>	-	Phosphoric acid
P	-	Phosphorus

$P_2O_5$	-	Phosphorus pentoxide
p	-	Pico ( $10^{-12}$ )
h	-	Planck constant
$r_p$	-	Polaron radius
$\varphi$	-	Porosity
$\tau_R$	-	Radiative lifetime
$A_R$	-	Radiative transition probability
$C_{RE}$	-	Rare-earth ion concentration
$\epsilon'$	-	Real part of the complex dielectric constant
$n$	-	Refractive Index
$\delta_{rms}$	-	Root-mean-square deviation
$S_\gamma$	-	Series where $\gamma$ is 1 or 2 or 3
Ag	-	Silver
AgCl	-	Silver Chloride
$\chi$	-	Spectroscopic quality factor
c	-	Speed of light
$\sigma_p^E$	-	Stimulated emission cross-section
S	-	Sulfur
$\Delta\lambda_{eff}$	-	The effective emission bandwidth
$\pi$	-	The mathematical constant (3.14)
$m_t$	-	The tangent slope value for the absorption edge.
d	-	Thickness
$J$	-	Total angular momentum
$A_T$	-	Total radiative transition probability
$\Delta E$	-	Urbach energy
$\lambda$	-	Wavelength
$I_p$	-	Wavelength of the PL peak
$\nu$	-	Wavenumber
$c_t$	-	Y-axis intercept value by the absorption edge tangent
Zn	-	Zinc
$ZnSO_4$	-	Zinc sulfate

## LIST OF ABBREVIATIONS

A.U.	-	Absorption Unit
Aq.	-	Aqueous
a.u.	-	Arbitrary unit
BO	-	Bridging Oxygen
CPE	-	Constant Phase Element
CR	-	Cross Relaxation
deg.	-	Degree
eV	-	Electron Volt
EDX	-	Energy Dispersive X-Ray
ET	-	Energy Transfer
Eq.	-	Equation
FTIR	-	Fourier Transform Infrared
FWHM	-	Full Width at Half Maximum
GCNCs	-	Glass-Ceramic Nanocomposites
GCs	-	Glass-Ceramics
HRTEM	-	High Resolution Transmission Electron Microscopy
IS	-	Impedance Spectroscopy
LCR	-	Inductance Capacitance Resistance
IR	-	Infrared
IFFT	-	Inverse Fast Fourier Transform
J-O	-	Judd-Ofelt
LFP	-	Lattice Fringe Profile
LFE	-	Local Field Enhancement
LSPR	-	Localized Surface Plasmon Resonance
MR	-	Multi-Phonon Relaxations
NCs	-	Nanocomposites
NPs	-	Nanoparticles
NIR	-	Near Infrared
NBO	-	Non-Bridging Oxygen
NR	-	Non-Radiative

PL	-	Photoluminescence
REIs	-	Rare Earth Ions
X–R	-	Reactance–Resistance
Ref.	-	Reference
RQ	-	Resistance- Constant phase element
SAED	-	Selected Area Electron Diffraction
SPR	-	Surface Plasmon Resonance
TEM	-	Transmission Electron Microscopy
UV	-	Ultraviolet
Vis	-	Visible
XRD	-	X-Ray Diffraction
XPS	-	X-Ray Photoelectron Spectroscopy

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# CHAPTER 1

## INTRODUCTION

### 1.1 Research Background

The main feature that distinguishes rare-earth elements from other elements is an incompletely filled 4f subshell that is screened by the completely filled outer 5s and 5p subshells [1]. Thus, when they are incorporated into any host material, rare-earth ions (REIs) gives rise to major absorption and emission actions responsible for a wide range of applications including lasers, light emitting diodes (LEDs), and amplifiers [2–4]. Absorption and emission cross-section of REIs are critical parameters deciding the REI's lasing potency. Therefore, the efforts have continually been made to improve the stimulated emission cross-section of REIs via the selection of appropriate host materials, suitable modifiers, and sensitizers (e.g., metal nanoparticles and nanostructures) [5–7].

Among the ternary and quaternary oxide hosts, the phosphate-based glass and glass-ceramic (GC) systems are potential because of their high thermal expansion coefficient, low phonon energy, large intake of REIs and low glass transition temperature [7–10]. Phosphate-based GCs have been acknowledged for better REIs luminescence features than glasses [11,12]. However, phosphate-based systems tend to absorb moisture, leading to the inclusion of  $\text{OH}^-$  impurities in the network structure which induce the undesirable non-radiative mechanisms in the system [13]. To overcome this limitation, the incorporating of some network modifiers was proved to be prospective to improve the chemical durability of phosphate glasses.

The combination of the phosphate and borate units enhance both the glass forming ability and the chemical durability of phosphate glasses by cross-linking phosphate chains [14]. The chemical durability and structural stability of phosphate glass can further be improved by adding  $\text{Zn}^{2+}$  ions in the network structures [15,16]. It

has also been argued that the interactions between the phosphate and sulfate ions can enhance the chemical durability and create a good environment for the intake of large number of REIs, allowing the fabrication of the miniaturized lasers with the improved features [17–19]. It is worth mentioning that the zinc-sulfo-boro-phosphate composition is a new promising host for the REIs doping.

The holmium ions ( $\text{Ho}^{3+}$ ) among various REIs have been used in diverse technologies including lasers [20]. They exhibit unique emissions in the ultraviolet (UV), visible (Vis), and infrared (IR) regions, however, the intensities of these emissions still need to be improved for glass lasers and nanophotonic devices [6]. To evaluate the  $\text{Ho}^{3+}$  radiative properties, calculations based on Judd-Ofelt theory have been widely used [2,3,5,7,21,22] over last few decades. Through these calculations, some essential parameters can be estimated including the stimulated emission cross-section ( $\sigma_p^E$ ). However,  $\text{Ho}^{3+}$  alike other REIs has small emission cross-section in amorphous hosts, causing high laser threshold and low gain [8]. Therefore, more studies to improve the  $\text{Ho}^{3+}$  emission cross-section are required. In this regard, some strategies have been used in order to enhanced the  $\sigma_p^E$  of  $\text{Ho}^{3+}$  such as the rightly selection of the host material, the co-doped with another REIs [5], and insertion of metallic nanoparticles (NPs) [7]. However, the exploration of the lasing potency of  $\text{Ho}^{3+}$  inside Ag NPs-sensitized phosphate-based GCNCs remain deficient.

Recently, a combination of the metal NPs with REIs in various host matrices has been proven to be advantageous for achieving the significant enhancement in the emission cross-section of the REIs. The Ag NPs being the common plasmonic metamaterial with abundance, strong biocompatibility, high chemical stability and resistant against oxidation has been used as the sensitizing agent in many systems to amplify the REIs lasing action [7,23–25]. The localized surface plasmon resonance (LSPR) effect of metal NPs has been demonstrated to be responsible for such significant enhancement of the optical properties [26,27]. Ag NPs size dependent improvement of LSPR field plays a vital role in enhancing the REIs photoluminescence (PL) emission intensity. The size can be controlled by means of altering the temperature and duration of thermal processing. In regard to this fact, controlling and exploring all the stages of Ag NPs formation including the starting

stage is required. Furthermore, the relative permittivity between the host material and the surface of the NP (dielectric-metal interface) play a significant role to achieve an enhancement in the PL intensity through the LSPR mediation.

The impedance spectroscopy has recently been proven to be a powerful tool to evaluate the complex permittivity and the microstructures [28]. This in turn provides a better understanding of the appropriate selection of the host matrix to improve the spectral attributes of REIs. In addition, most of the reported literatures [17,28,29] on the structural, and impedance correlation in phosphate-based systems free of REIs. However, by ascertaining such relationship in the REIs doped glasses or GCs an in-depth understanding of the microscopic mechanisms can be developed.

Based on this background, this thesis took an attempt to evaluate the structural, microstructural, impedance and optical characteristics of the Ag NPs (varied size) and  $\text{Ho}^{3+}$  co-doped zinc-sulfo-boro-phosphate GCs nanocomposites (GCNCs). The main goal is to determine the lasing potency of  $\text{Ho}^{3+}$  in the newly composed system.

## **1.2 Problem Statement**

The more the change between the local surroundings of all  $\text{Ho}^{3+}$  distributed in the phosphate-based system, the broader the spectral peaks. This in turn lowers the stimulated emission cross-section that needs to be enhanced for high optical gain laser applications. The optimum composition with efficient lasing action is required and remains an open problem. Creating some crystalline domains within the glassy matrix is believed to attain strong optical response. Interestingly, the mechanism of Ag NPs (varying size and contents) that enables LSPR assisted lasing potency in phosphate-based nanocomposites is critical to obtain the optimum composition. The composition optimization is pre-requisite to determine the modified overall properties. Therefore, the optimization of  $\text{Ho}^{3+}$  as well as Ag NPs concentration inside the phosphate-based nanocomposites need to be systematically carried out.

The lasing potency of  $\text{Ho}^{3+}$  doped various host materials are primarily determined by their surrounding structures and microstructures. Thus, detail analyses are required in order to understand these basic quantities. Over the years, although diverse studies have been carried out on  $\text{Ho}^{3+}$ -activated host matrices, seldom studies have focused on its structural, microstructural, impedance and optical properties in zinc-sulfo-boro-phosphate nanocomposite for the development of  $\text{Ho}^{3+}$  based inexpensive, visible and eye-safe laser.

It is known that the Judd-Ofelt (J-O) analyses are important tools to understand the host material and the structural properties surrounding the REI as well as to determine the lasing potency via some radiative parameters. Stimulated emission cross section is the most critical parameter to decide the feasibility of achieving efficient lasing action. However, the J-O intensity and radiative parameters for  $\text{Ho}^{3+}$ -activated phosphate-based nanocomposite with Ag NPs sensitization has not yet been explored in-depth.

Interestingly,  $\text{Ho}^{3+}$  has several close-lying excited energy levels over the visible spectral region responsible for intense visible spectral transitions. However, the non-radiative processes associated with various relaxational mechanisms of these excited states lead to energy loss often limit practical applications of holmium. To surmount such shortcomings, based on the fact that is the electrical field of the host environment plays a role in the 4f energy level splitting to several sublevels, a better understanding on the appropriate selection of the host matrix is necessary. To achieve this perspective, a basic knowledge on the structure and microstructure of the chosen host material is mandatory. In this spirit, the impedance analysis is often recommended to provide useful information about the network microstructure, alongside with some impedance properties. This in turn, can be used to elucidate the relaxation mechanisms concerning the carriers transport properties in the materials under study. Therefore, detail studies on the structural, microstructural, impedance and optical properties of  $\text{Ho}^{3+}$ -activated phosphate-based nanocomposites with and without the presence of Ag NPs need to be determined so that a possible correlation amid the abovementioned traits can be established.

### 1.3 Research Objectives

Based on the above problem statement, the following objectives are set.

- (a) To optimize the composition of  $\text{Ho}^{3+}$ -activated zinc-sulfo-boro-phosphate GC system without and with Ag NPs sensitization.
- (b) To determine the influence of  $\text{Ho}^{3+}$  content on the structural, microstructural and optical properties of the proposed GCs and GCNCs.
- (c) To evaluate the lasing potency of the optimum GCNC (sample with highest PL intensity from each series) via Judd-Ofelt intensity and radiative parameters for supporting the experimental optical data.
- (d) To correlate the structural, microstructural, impedance and optical properties of the proposed GCs and GCNCs.

### 1.4 Scope of Research

To achieve the set objectives, the following scopes are included.

- (a) Selection of appropriate amount of chemicals for every 20 gram batch in three series of samples. The first GCs series is composed with varying  $\text{Ho}_2\text{O}_3$  content and without Ag NPs embedment, while the second and third GCNCs series are formulated with changing Ag NPs concentration (Ag NPs of different mean size) at fixed  $\text{Ho}^{3+}$  content.
  - $(40-x) \text{P}_2\text{O}_5 - 30 \text{B}_2\text{O}_3 - 30 \text{ZnSO}_4 - x \text{Ho}_2\text{O}_3$ , ( $x = 0.0, 0.2, 0.4, 0.5, 0.6, 0.8$  and  $1.0 \text{ mol}\%$ ).
  - $(40-x-y) \text{P}_2\text{O}_5 - 30 \text{B}_2\text{O}_3 - 30 \text{ZnSO}_4 - x \text{Ho}_2\text{O}_3 - y \text{Ag nanopowder}$ , ( $x =$  the best mol% selected from (1) with highest PL intensity in visible spectral region.  $y = 0.6, 0.7, 0.8$  and  $0.9 \text{ mol}\%$ ).

- $(40-x-z) \text{P}_2\text{O}_5 - 30 \text{B}_2\text{O}_3 - 30 \text{ZnSO}_4 - x \text{Ho}_2\text{O}_3 - z \text{AgCl}$ , ( $z = 0.6, 0.7, 0.8$  and  $0.9$  mol%).
- (b) Preparation of the mentioned three series of samples using melt quenching method.
  - (c) Determination of sample density by Archimedes method.
  - (d) Characterization of the structural features using XRD measurement, FTIR, Raman, XPS, EDX spectroscopies.
  - (e) Determination of the microstructure characteristics by:
    - HRTEM that further identifies the existence (and morphology) of the nanoparticles.
    - IS that provides the supportive impedance data.
  - (f) Characterization of optical (absorption and emission) features using UV-Vis-NIR and PL spectroscopies.
  - (g) Assessment of the lasing potency of the synthesized optimum nanocomposites containing both  $\text{Ho}^{3+}$  and Ag NPs using J-O analysis (in terms of intensity and radiative parameters).

## 1.5 Significance of Research

- (a) New nanocomposites with optimum composition have been produced as an alternative solid-state lasing media with relatively strong lasing potency that may be useful for the devolvement of various nanophotonic devices.
  - The obtained large values of the branching ratio and respective stimulated emission cross-section ( $73.88\%$  and  $46.68 \times 10^{-21} \text{ cm}^2$  for the green; and  $83.97\%$  and  $41.12 \times 10^{-21} \text{ cm}^2$  for the red) were greater than most of the

state-of-the-art reports indicated the effectiveness of the proposed samples for the construction of green and red lasers.

- The attained strong lasing potency of the IR transition (branching ratio: 71.40%; stimulated emission cross-section:  $36.95 \times 10^{-21} \text{ cm}^2$ ) demanded for many photonic applications was greater than the existing one (comparative evaluations were given hereinafter in page 120).
- (b) New knowledge has been generated on the relationship among structural, impedance and optical properties in the studied nanocomposites. The optical properties can be modified by developing such correlations. For instance, the polarons that were responsible for the conduction mechanism might play a significant role in the ET mechanism.
- (c) The mechanism of the Ag NPs localized surface plasmon resonance and its influence on the enhancement of the radiative properties of  $\text{Ho}^{3+}$  in the titled system has been better understood where the impact of embedding Ag NPs with two different sizes on the  $\text{Ho}^{3+}$  transitions (while maintaining the local structure relatively fixed) was explored for the first time.

## 1.6 Thesis Outline

The thesis is organized as follows: Chapter 1 presents the background of the study, statement of the problems, research objectives, scope of the research and its significance. Chapter 2 provides an overview of the previous related literature. Chapter 3 displays the research methodology. Chapter 4 represents and discusses the research results. Finally, chapter 5 summarizes the findings with respect to the set research objectives, as well as some future research suggestions.

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## LIST OF PUBLICATIONS

### (a) ISI Journals

- **Publication:** Alqarni, Areej S., Hussin, R., Alamri, S.N. and Ghoshal, S.K., 2019. Intense red and green luminescence from holmium activated zinc-sulfo-boro-phosphate glass: Judd-Ofelt evaluation. *Journal of Alloys and Compounds*, 808, p.151706. Available at: <https://doi.org/10.1016/j.jallcom.2019.151706>.
- **Publication:** Alqarni, Areej S., Hussin, R., Alamri, S.N. and Ghoshal, S.K., 2020. Tailored structures and dielectric traits of holmium ion-doped zinc-sulpho-boro-phosphate glass ceramics. *Ceramics International*, 46(3), pp.3282–3291. Available at: <https://doi.org/10.1016/j.ceramint.2019.10.034>.
- **Publication:** Alqarni, Areej S., Hussin, R., Alamri, S.N. and Ghoshal, S.K., 2020. Spectral features of Ho<sup>3+</sup> -doped boro-phosphate glass-ceramics: Role of Ag nanoparticles sensitization. *Journal of Luminescence*, 223, p.117218. Available at: <https://doi.org/10.1016/j.jlumin.2020.117218>.
- **Publication:** Alqarni, Areej S., Hussin, R., Alamri, S.N. and Ghoshal, S.K., 2020. Ag nanoparticles localised surface plasmon field regulated spectral characteristics of Ho<sup>3+</sup> -doped phosphate-based glass-ceramic. *Results in Physics*, 17(April), p.103102. Available at: <https://doi.org/10.1016/j.rinp.2020.103102>.
- **Publication:** Alqarni, Areej S., Hussin, R., Alamri, S.N. and Ghoshal, S.K., 2020. Customized physical and structural features of phosphate-based glass-ceramics: role of Ag nanoparticles and Ho<sup>3+</sup> impurities. *Journal of Taibah University for Science*, 14(1), p. 954-962. Available at: <https://doi.org/10.1080/16583655.2020.1791536>.

(b) Other Contributions

- **Conference:** Alqarni, Areej S., Hussin, R., and Ghoshal, S.K., 2019. Modified Structure and Impedance Attributes of Holmium Ions Included Phosphate-Based Media: Synergism of Amorphous and Crystalline Phases. *Proceeding of Sixth Academic Conference on Natural Science*, Thai Nguyen University, Vietnam. ISBN 978-604-913-088-5.
- **Conference:** Alqarni, Areej S., Hussin, R., Alamri, S.N. and Ghoshal, S.K., 2020. A New Host with Customized Intense Lasing Action: Ag Nanoparticles and  $\text{Ho}^{3+}$  Interplay. *Proceeding of International Conference on Physics and Chemistry of Materials in Novel Engineering Applications*, Coimbatore, India. <https://doi.org/10.1063/5.0019893>