EFFECT OF SILVER NANOPARTICLES ON OPTICAL PROPERTIES OF ERBIUM-DOPED MAGNESIUM PHOSPHATE GLASS

MUHAMMAD JUNAID AMJAD

UNIVERSITI TEKNOLOGI MALAYSIA

EFFECT OF SILVER NANOPARTICLES ON OPTICAL PROPERTIES OF ERBIUM-DOPED MAGNESIUM PHOSPHATE GLASS

MUHAMMAD JUNAID AMJAD

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Doctor of Philosophy (Physics)

Faculty of Science
Universiti Teknologi Malaysia

OCTOBER 2013

To my beloved parents
for their enduring love, motivation and support

ACKNOWLEDGEMENT

Alhamdulillah, I am greatly indebted to Allah SWT on His mercy and blessing for making this research a success.

I would like to acknowledge the advice and guidance of Prof. Dr. Md. Rahim Sahar. As my supervisor, he always aimed to encourage me to investigate through the experiments and to understand the truth of the science. His advices on the morality and affability are certainly expensive lessons for me.

I also would like to acknowledge the supervision from my co-supervisor, Assoc. Prof. Sib Krishna Ghoshal. Indeed, he persuades me toward deeper investigation on both theoretical and experimental assignments. The special thanks to him to show me the best academic lifestyle as well as academic communications.

I sincerely thank all the lecturers who have taught me, for the lesson that has been delivered. Not to mention, to my fellow postgraduate friends especially M. R. Dousti, thank you for sharing useful ideas, information and moral support during the course of study.

Last but not least I would like to express my appreciation and gratitude to my parents, sisters and brother for all the supports and encouragements they provide during my studies.

ABSTRACT

Three series of phosphate glass with composition (59.5-x)P_2O_5-40MgO-xAgCl-0.5Er_2O_3 ($0.0 \leq x \leq 1.5$ mol%), (59.5-x)P_2O_5-40MgO-xAgCl-1.5Er_2O_3 ($0.0 \leq x \leq 1.5$ mol%) and (69.7-x)P_2O_5-30MgO-0.3Er_2O_3-xAgCl, where x=0 or 0.5 mol% were prepared using melt quenching technique. The amorphous nature of the glass was confirmed using the X-ray diffraction (XRD) method. The homogeneous distribution of spherical Ag nanoparticles (NPs) (average size of 37 nm) in the glassy matrix was evidenced from the transmission electron microscopy (TEM) analyses. The UV-VIS-NIR absorption spectra showed 7 bands corresponding to $^4I_{13/2}$, $^4I_{11/2}$, $^4I_{9/2}$, $^4F_{9/2}$, $^4S_{3/2}$, $^2H_{11/2}$, $^4F_{7/2}$ transitions. The absorption spectrum of Er^{3+} ions free glass sample containing Ag NPs displayed a prominent surface plasmon resonance (SPR) band located at ~528 nm. The infrared to visible frequency up-conversion (UC) emission under 797 nm excitation showed two emission bands of green ($^4S_{3/2}$-$^4I_{15/2}$) and red ($^4F_{9/2}$-$^4I_{15/2}$) corresponding to Er^{3+} transitions. An enhancement in UC emission intensity of both green and red bands was observed in the presence of silver NPs either by increasing annealing time or by NPs concentration. The enhancement of UC emission was understood in terms of the intensified local field effect due to silver NPs. For first series of samples, the Judd-Ofelt parameters (Ω_2, Ω_4 and Ω_6) were calculated and were found to lie in the range (8.05-9.20) $\times 10^{-20}$ cm^2, (2.00-2.58) $\times 10^{-20}$ cm^2 and (1.05-2.30) $\times 10^{-20}$ cm^2 respectively. These parameters were used to estimate the important parameters such as radiative transition probability (A), stimulated emission cross-section (σ_P^E), radiative life time (τ_R) and branching ratio (β_R) for the excited levels of Er^{3+} ions in the glass. Furthermore, the value of Ω_2 for the studied glasses was found to be higher than that of glasses reported in the literature. These relatively higher values of Ω_2 reflect low symmetry and high covalency around the Er^{3+} ions. These phosphate glass nanocomposites can be potentially used as photonic and plasmonic materials.

ABSTRAK

Tiga siri kaca fosfat dengan komposisi $(59.5\text{-}x)P_2O_5\text{-}40MgO\text{-}(x)AgCl\text{-}0.5Er_2O_3$ ($0.0 \leq x \leq 1.5$ mol%), $(59.5\text{-}x)P_2O_5\text{-}40MgO\text{-}(x)AgCl\text{-}1.5Er_2O_3$ ($0.0 \leq x \leq 1.5$ mol%) dan $(69.7\text{-}x)P_2O_5\text{-}30MgO\text{-}0.3Er_2O_3\text{-}(x)AgCl$, dengan x = 0 atau 0.5 mol% telah disediakan menggunakan teknik pelindapan leburan. Sifat amorfus kaca telah ditentusahkan menggunakan kaedah pembelauan sinar-X (XRD). Zarah sfera Ag bersaiz nano dengan saiz purata 37 nm di dalam matrik kaca yang tertabur secara homogen dapat dilihat di bawah melalui mikroskop transmisi elektron (TEM). Spektra penyerapan UV-VIS-NIR menunjukkan tujuh jalur yang berpadanan dengan transisi $^4I_{13/2}$, $^4I_{11/2}$, $^4I_{9/2}$, $^4F_{9/2}$, $^4S_{3/2}$, $^2H_{11/2}$, $^4F_{7/2.}$ Spektrum penyerapan kaca tanpa Er^{3+} menghasilkan jalur resonan plasmon permukaan (SPR). *Up-conversion* (UC) pada julat lembayung boleh nampak di bawah pengujaan 797 nm menunjukkan adanya dua jalur pancaran iaitu hijau ($^4S_{3/2}$-$^4I_{15/2}$) dan merah ($^4F_{9/2}$-$^4I_{15/2}$). Pertambahan keamatan pancaran UC bagi kedua-dua warna hijau dan merah dapat dicerap dengan kehadiran zarah nano Ag sama ada dengan pertambahan masa sepuhlindap atau pertambahan kepekatan zarah nano. Pertambahan pancaran UC dapat difahami kerana terdapatnya kesan medan setempat disebabkan oleh zarah nano Ag. Untuk siri sampel pertama, parameter Judd-Ofelt (Ω_2, Ω_4 and Ω_6) telah dihitung dan didapati masing-masing bernilai dalam julat $(8.05\text{-}9.20)\times10^{-20}$cm^2, $(2.00\text{-}2.58)\times10^{-20}$ cm^2 dan $(1.05\text{-}2.30)\times10^{-20}$ cm^2. Parameter ini kemudian digunakan untuk menganggarkan kebarangkalian peralihan radiatif (A), keratan rentas pancaran terangsang (σ_P^E), jangka hayat radiatif (τ_R) dan nisbah cabangan (β_R) untuk aras tenaga teruja dalam kaca. Tambahan lagi, nilai Ω_2 bagi kaca yang dikaji didapati lebih tinggi berbanding dengan kaca lain yang dilaporkan. Nilai Ω_2 yang secara relatifnya lebih tinggi mencerminkan simetri yang rendah dan sifat kovalen yang tinggi di sekeliling ion Er^{3+}. Komposit nano kaca fosfat berpotensi untuk digunakan sebagai bahan fotonik dan plasmonik.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

A/D	-	Analog to Digital
CET	-	Co-operative Energy Transfer
CR	-	Cross Relaxation
CUC	-	Cooperative Upconversion
CW	-	Continuous Wave
ET	-	Energy Transfer
EDFA	-	Erbium Doped Fiber Amplifiers
EDX	-	Energy Dispersive X-ray
ESA	-	Excited States Absorption
ESR	-	Electron-Spin Resonance
FTIR	-	Fourier Transform Infrared
FWHM	-	Full width at Half Maximum
GSA	-	Ground State Absorption
HR	-	High-Resolution
IR	-	Infrared
JO	-	Judd-Ofelt
LSPR	-	Localized Surface Plasmon Resonance
LRE	-	Lightening Rod Effect
NMR	-	Nuclear-Magnetic Resonance
NP	-	Nanoparticle
NR	-	Non-Radiative
OD	-	Optical Density
PL	-	Photoluminescence
PLE	-	Photoluminescence Excitation
RGB	-	Red-Green-Blue
RE	-	Rare Earth
SEFS	-	Surface Enhanced Fluorescence Spectroscopy

SEM	-	Scanning Electron Microscope
SERS	-	Surface Enhanced Raman Spectroscopy
SFM	-	Scanning force microscopy
SHG	-	Second Harmonic Generation
SPM	-	Scanning Probe Microscopy
SPR	-	Surface Plasmon Resonance
TEM	-	Transmission Electron Microscope
THG	-	Third Harmonic Generation
TL	-	Thermal Lens
UC	-	Upconversion
UTM	-	Universiti Teknologi Malaysia
UV	-	Ultraviolet
VIS	-	Visible
WDM	-	Wavelength Division Multiplexing
XRD	-	X-Ray Diffraction
RMSE	-	Root Mean Square Error

LIST OF SYMBOLS

ρ_{ext} - External Charge

2θ - Angle of Diffraction

A - Radiative Probability

B - Magnetic Induction

c , v_0 , v' - Speed of Light

d - Dilectric Displacement

D - Size of Nanoparticle

d_{Er} - Inter-Nuclear Distance Between Er-Er Ions

d_{EA} - Inter-Nuclear Distance Between Ag and Er Ion

d_{Ag} - Inter-Nuclear Distance Between Ag-Ag Particles/Ions

e - Charge of Electron

E - Electric Field

E_{dir} - Direct Optical Band Gap

E_{ind} - Indirect Optical Band Gap

ΔE, E_U - Urbach Energy

E_η - Activation Energy

F - Oscillator Strength

H - Magnetic Field

I - Intensity

J_{ext} - Current Densities

K - Wave vector

Ƙ - Extinction Coefficient

L - Diameter of Nanoparticle

l - Length

l_i - Orbit Angular Momentum

m - Mass of Electron

n, n' - Refractive Index

N - Density of the Electrons

n_2 - Non-linear Refractive Index

M - Average Molecular Weight

N_c - Concentration

N_A - Avogadro’s number

P - Volume Fraction of the Silver Spheres

R - Glass Constant

R_i - Reflection Loss

R' - Refractivity

S - Stability Factor

S_{ed} , S_{md} - Electric and Magnetic Dipole Linestrengths

T' - Transmission

T - Temperature

T_c - Crystallization Temperature

T_g - Glass Transition Temperature

T_m - Melting Temperature

t - Time

$||\mathrm{U}^{(t)}||^2$ - Reduced Matrix Elements

$\mathrm{u_F}$ - Fermi Energy

V - Molar Volume

V_p - Volume of Particle

V_a - Mean Molar Volume

V_{EM} - Hamiltonian of Interaction of Light by Ion

W - Weight

W_{ph} - Photon Cut-off Energy

Z^* - Effective Nuclear Charge

α - Absorption Co-efficient

α_m - Polarizability

β - Branching Ratio

ε - Dielectric Function

ε_0 - Permittivity of Vacuum

h - Plank’s Constant

$X^{(i)}$ - Susceptibility

ρ - Density of glass

σ_{emi} - Emission Cross-Section

σ_{dc} - Direct Current Conductivity

Γ - Damping Constant

Ω_i - Judd-Ofelt Intensity Parameters

λ - Wavelength

Φ - Heating Rate

$\zeta(r_i)$ - Spin-Orbit Coupling Efficiency

Γ - Surface Free Energy per Unit Area

τ - Lifetime

η - Enhancement Factor

v_d - Abbe Number

Ω - Frequency

ω_P - Frequency of Plasma

$|(S,L)J>$ - Electronic State of an Element Defined by its Spin, Orbital and Total Momentums

σ_P^E - Stimulated Emission Cross-section

$\Delta\lambda_{eff}$ - Effective Band width

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Introduction

Glass is a non-crystalline solid material that exhibits a glass transition. It is typically brittle and usually transparent. Phosphate glass is a type of optical glasses that consists of metaphosphates of different metals. As appears from the name in phosphate glass, the glass former is P_2O_5 and it can be used with different modifiers such as magnesium oxide (MgO), aluminum oxide (Al_2O_3) etc. Usually, P_2O_5 crystallizes in four forms. The most common consists of P_4O_{10}.

Phosphate glasses can be used as laser gain media, in the form of optical fibers or in bulk lasers. They have their unique advantage of accepting a high concentration of rare-earth (RE) ions such as Er^3, Yb^{3+} and Nd^{3+} without any unwanted effects such as clustering or quenching etc.

Optical properties and functionalities of metallic nanostructures are different from those of bulk therefore they have got considerable attention [1-4]. Since in bulk metals there is no separation between conduction and valence bands, hence electrons are least confined producing the conducting behaviour of the metal. In case of nanostructures, due to the decrease in the size the electrons are more confined hence the metallic nature converts into semiconducting and then into insulating. During these transformation regimes, many novel characteristics are likely to happen which are noticeable.

Surface plasmon resonance is a phenomenon in which free electrons are collectively excited from one surface of the metallic nanoparticle (NP) to the other. Plasmonics is the new rapidly growing branch of science in which optical behavior as well as the potential applications of metallic nanostructures are analyzed and understood [4]. In photoluminescence of lanthanides ions the excitation energy is converted into emission energy which is the major principle for the modern technologies such as solid state lasers, optical communications, sensing and display systems etc.

Understanding and quantifying the upconversion (UC) luminescence in rare earth (RE) doped phosphate glasses is receiving special attention due to the potential application in full color display, laser antiforgery and bio-label to cite a few [5-11]. The UC efficiency critically depends on host matrix and the amount of doped rare earth ion that may be altered by eight orders of magnitude in different matrix. Therefore, the choice of appropriate host matrix is crucial for efficient UC luminescence [8]. The chemical durability of the phosphate glasses becomes comparable with the silicate glasses when additional network forming oxides and one or more network modifying oxides are added to them [11, 12]. In addition to good mechanical and thermal stability the optical properties of phosphate glasses include excellent transparency [13]. These favorable features make phosphate glasses useful in optical devices. Moreover, phosphate matrix can dissolve considerable amounts of alkaline earth, transition metal and RE ions [14].

In solids, RE ions can be excited under ultraviolet (UV) excitation either by charge transfer states (CTS) transitions [15] or by host excitation induced energy transfer [16]. For majority of the RE-doped glasses, whole of the energy is nearly lost to the glass matrix therefore this process has a low efficiency, consequently most RE-doped glasses under high energy UV radiation excitation are low-efficiency phosphors. Substantial amount of literature exists on the study of nanometer-sized metal particles in glasses because of their non-linear properties including magnetism [17], optical non-linearity [18] and electrical properties [19]. The presence of quantum size behavior is attractive due to its applicability in photonic devices. Understanding the mechanism of interaction between the metallic NPs and the rare earth ions is prerequisite for the development of photonic devices. Phenomena of interaction of light with rare earth doped glasses embedded with metallic NPs is gaining paramount importance due to the possibility of applications ranging from surface-enhanced Raman spectroscopy to metal-enhanced luminescence [20-22]. The small absorption cross-section of most of the RE ions requires ways to increase it for applications. One way is to achieve it by energy transfer from a species with a large absorption cross-section to the rare earth ions. The other route is by using two or more rare earth ions together or by using rare earth ions with metallic NPs [23]. Avoiding the concentration quenching effect to get enhanced optical properties, glasses containing small amount of rare earth ions embedded with metallic NPs are found to be favourable.

Phosphate based glasses can be used in many applications such as optical data transmission, sensing and laser technologies [24]; therefore they are widely studied recently. Among the different characteristics of phosphate glass, some of them are high transparency, low dispersion, high solubility for RE ions and low glass transition temperature etc. [25].

These glasses can be used for hermetic sealing technology [26, 27] due to their low glass transition temperature and large thermal expansion co-efficient compare to silicate glasses. Additionally, phosphate glasses are recommended as solid state ionic conductors and laser hosts [28]. The study of optical properties of RE ions in low-dimensional semiconductors is primarily focused in recent years due to their applications in optoelectronic devices [29-33]. The excitation of RE ions is proposed to occur due to the recombination of photo generated carriers that results the energy transfer to RE ions in or near the nanocrystal.

For the upconversion fluorescence, among the rare earth ions, Er^{3+} is the most widely used as well as one of the most efficient ions [34]. Due to the ability of the NPs to control the optical fields on the nanometer scale they are of great interest. The optical properties of plasmon resonance, such as peak wavelength, full-width at half maximum (FWHM) depend on the material, size, shape and structure of the NPs, as well as on the surrounding media [35]. Interestingly, the observation of surface enhanced Raman spectra and fluorescence enhancements [36, 37] geared up the study of optical properties of nanocomposite materials, such as Er^{3+} doped glasses containing small silver particles. Glasses doped with RE ions and metallic NPs have been investigated due to their applications as optical devices [38]. In RE doped glasses containing small metallic particles, any significant influence on the absorption and photoluminescence (PL) rate of the RE ions due to these small particles should be of electronic origin. The electromagnetic (EM) mechanism which is produced by plasmon excitation at the Mie resonance frequency can be regarded as an additional interaction due to the high field gradients nearby the metallic particles. However, in order to avoid the concentration quenching and to make the devices with enhanced optical properties, the concentration of the RE has to be low enough. One possible route of minimizing this quenching effect is to modify the environment felt by the RE ion [39-41]. Therefore, glasses containing the small amount of RE ions embedded with metallic NPs are of considerable interest, because the luminescence efficiency may increase many times when the optical frequency of the excitation beam and/or the luminescence frequency are near resonance with the surface plasmon frequency of the NPs [42]. This enhancement is due to the large local field acting on the ions positioned near the NPs.

The luminescence [42-47] and non-linear properties [42, 48-50] of glasses containing both RE and metallic nanoparticles (NPs) can be enhanced due to the presence of these nanostructures. There is a further enhancement in the emission when the excitation beam wavelength becomes in resonance with the plasmon wavelength of the NPs [51, 52].

It is well known that for the enhancement in the luminescence efficiency, there should be an optimum distance between the NPs and RE ions. If the distance between them is very small, then quenching can occur instead of enhancement.

Nevertheless one negative aspect of phosphate based glasses is their hygroscopicity, due to which the quantum efficiency (QE) of RE ions can be rigorously affected. The atmospheric moisture and the starting materials are the causes of inclusion of hydroxyl group but can be minimized by changing the composition and preparation method [53-55].

1.2 Background

Due to the exceptional optical properties of RE ions and their photonic applications, nonradiative energy transfer processes involving these ions in solids have been vastly studied. Generally certain applications (such as the mechanism of anti-stokes emitters) are supported by energy transfer (ET) processes however, in the case of RE based lasers it is unfavourable because laser threshold may be increased by the interactions among the active ions.

Specifically, the study of ET mechanism in glasses having frequency gap in the visible region has earned large attention because some glasses may present efficient visible luminescence when doped with RE ions. Due to many reasons phosphate based glasses are a good choice to study these effects, some of which includes large transmittance window (from the visible to the infrared region), low cutoff phonon energy, high refractive index (~2.0) and large chemical stability.

Presence of NPs inside the glass matrix containing RE ions can enhance the luminescence efficiency as reported by many authors [56-59]. In all the cases this enhancement is attributed to the large local field on the RE ions present within the vicinity of metallic NPs and by the energy transfer from metallic NPs to the RE ions.

The introduction of semiconducting and metallic NPs in RE doped glasses have been utilized to enhance the luminescence intensity provided that the excitation or luminescence wavelength is near to the surface plasmon resonance (SPR) wavelength for metallic NPs and must be greater than optical band gap energy for semiconducting NPs respectively. For instance Malta *et. al* [60] reported enhancement in Eu^{3+} luminescence in a fluoroborate glass with silver NPs in 1985.

In nanophotonics this approach of getting enhanced luminescence is getting renewed attention. However in literature only few glasses are studied such as tellurium and germanate based glasses and not many examples of other glasses being investigated by this approach. Furthermore, for luminescence enhancement by the effect of surface plasmon, chalcogenide glasses based on chalcogen elements: S, Se, and Te generally mixed with elements such as Ge, Ga, Sb, As, etc. are important candidates.

On the other hands only few reports are found on metallic NPs embedded, RE doped phosphate glasses. The matrices where the phenomenon of enhanced luminescence is observed are usually silicate or tellurite glasses. On the contrary phosphate glass which is widely used in photonic applications mainly because of its advantageous mechanical properties and ability to accept higher concentration of RE ions is not much exploited in the field of plasmonics or nanophotonics. Especially no report is found in the literature in which metallic NPs are embedded inside the phosphate glass matrix with RE ions. This has motivated us to a deeper study into the effect of the matrix on such luminescence enhancement and energy transfer processes.

1.3 Problem Statement

To achieve enhanced optical characteristics in phosphate glasses, the concentration of RE ions should be low enough to avoid quenching effect. To enhance UC luminescence, many routes have been reported in the literature such as using two or more RE together or by doping metallic NPs with RE. Therefore glasses co-doped with metallic NPs and RE are of particular interest.

Inspite of many experiments on phosphate glasses the basic understanding on the unusual non-linear optical properties is still lacking. Consequently, the local field effect due to metallic NPs around the RE ions that possibly enhances the non-linear optical properties requires further investigation. However, there is a lack of systematic theory and not many experiments have been reported to explain the influence of embedded NPs in the erbium doped phosphate glass as well as influence of heat treatment. Also there is still lack of report on the effect of metallic NPs on Judd-Ofelt intensity parameters. Furthermore, there is insufficient data available in literature in which stimulated emission cross-section is calculated with and without metallic NPs and a comparison is made.

1.4 Objectives of the Study

Some of the objectives of the present study are

(i) To synthesize a series of RE doped phosphate glass samples with and without silver NPs by melt quenching method.

(ii) To characterize them using X-ray diffraction (XRD), transmission electron microscope (TEM) imaging, infrared (IR), UV-VIS and photoluminescence (PL) spectroscopy.

(iii) To determine Judd-Ofelt intensity parameters with and without silver NPs and make a comparison.

(iv) To determine stimulated emission cross-section with and without silver NPs and make a comparison.

(v) To explain the mechanism behind the variation in Er^{3+} luminescence.

1.5 Scope of the Study

A wide range of phosphate based glasses have been intensively studied. However, only a few reports have been found in the literature describing the effect of silver NPs on the optical properties of phosphate glass.

In this study the optical properties of magnesium-phosphate glass co-doped with Er^{3+} and silver NPs are studied. The glass is prepared with certain compositions with and without silver NPs. In addition, heat treatment is accomplished to analyze its influence on red and green emissions of Er^{3+}. The amorphous nature of the glass is investigated by XRD. The existence of silver NPs inside the glass host is confirmed by TEM analysis. Optical characterization is accomplished by PL and UV-VIS-NIR absorption spectroscopy.

The present study is highly relevant from applied viewpoint of technology for preparing better and efficient glasses having superior optical performances, with controlled dopants and NPs. This study is fundamentally important for understanding the mechanism responsible for structural and optical properties in nanoamorphous materials.

It is strongly believed that this systematic experimental methodology of careful sample preparation, spectroscopic studies and theoretical analysis could make accurate quantitative estimate regarding the nonlinear optical and structural behavior in these nanoglasses. Through these investigations the mechanism of the linear and nonlinear optical behaviors will be clearly understood.

1.6 Thesis Outline

A short introduction on the importance of metallic NPs embedded host glasses is presented in the first chapter along with specific objectives, in addition to these; significance and statement of the problem of the study have been discussed in this chapter. In chapter 2 literature review has been presented concisely. In chapter 3 the dealing of electromagnetic radiations with metal is discussed thoroughly as well as the introduction of plasmons is introduced. The spectroscopic properties of trivalent erbium (Er^{3+}) will be discussed. The energy level diagram of electronic arrangement of erbium ion will be explained and probable mechanisms such as energy transfer and relaxation processes will be clarified in chapter 3. In chapter 4 the experimental procedures to prepare and characterize the samples are given. Applied techniques to synthesize the glass samples will be established and various spectroscopic studies to investigate the optical properties of proposed samples will be introduced.

Chapter 5 will express the results of different analysis on phosphate glass samples doped with Er^{3+} ion and silver NPs. The analyses contain a range of experiments such as FTIR, UV-VIS-IR absorption and PL spectroscopy. The Judd-Ofelt theory is also applied according to theoretical study in chapter 3. The effect of heat treatment is given to establish a new method to enhance the effect of silver NPs by growing and nucleating them inside the glass matrix. A discussion to each study is followed in the same section.

Based on the results, given in 5th chapter, some conclusions are made which are presented in chapter 6 along with future recommendations. This dissertation will end by the list of published journal papers [Appendix A] and least square reduced fitting method [Appendix B].

REFERENCES

1. Schwartzberg, A. M. and Zhang, J. Z. Novel Optical Properties and Emerging Applications of Metal Nanostructures. *J. Phys. Chem. C.* 2008.112: 10323.
2. Lu, X., Rycenga, M., Skrabalak, S. E., Wiley, B. and Xia, Y. Chemical synthesis of novel plasmonic nanoparticles. *Ann. Rev. Phys. Chem.* 2009. 60: 167192.
3. Bäumer, M. and Freund, H. J. Metal deposits on well-ordered oxide films. *Prog. Surf. Sci.* 1999. 61: 127.
4. Ozbay, E. Plasmonics: merging photonics and electronics at nanoscale dimensions. *Sci.* 2006**.** 311**:** 189.
5. Matsuura, D. Red, green, and blue upconversion luminescence of trivalent-rare-earth ion-doped Y_2O_3 nanocrystals. *Appl. Phys. Lett.* 2002. 81: 4526.
6. Luo, X., Cao, W. and Sun, F. The development of silicate matrix phosphors with broad excitation band for phosphor-convered white LED. *Chin. Sci. Bull.* 2008. 53: 2923.
7. Wright, W.H., Rundle, G. A., Mufti, N. A., Yao,V. and Cooper, D.E. Flow cytometry with upconverting phosphor reporters. *Proc. SPIE*, 1998. 3260: 245.
8. Heer, S., Kömpe, K., Güdel, H. U. and Haase, M. Highly Efficient Multicolour Upconversion Emission in Transparent Colloids of Lanthanide-Doped $NaYF_4$ Nanocrystals. *Mater.* 2004. 16: 2102.
9. Corstjens, P. L. A. M., Li, S., Zuiderwijk, M., Kardos, K., Abrams, W. R., Niedbala, R. S. and Tanke, V. Infrared up-converting phosphors for bioassays nanobiotechnology. *IEEE Proc.* 2005. 152: 64.
10. Luo, X. and Cao, W. Blue, green, red upconversion luminescence and optical characteristics of rare earth doped rare earth oxide and oxysulfide. *Sci. China, Ser. B.* 2007. 50: 505.

11. Mazali, I. O., Barbosa, L. C. and Alves, O. L. Preparation and characterization of new niobophosphate glasses in the Li_2O-Nb_2O_5-CaO-P_2O_5 system. *J. Mater. Sci.* 2004. 39: 1987.

12. Teixeira, Z., Alves, O. L. and Mazali, I. O. Structure, Thermal Behavior, Chemical Durability, and Optical Properties of the Na_2O–Al_2O_3–TiO_2–Nb_2O_5–P_2O_5. Glass System. *J. Am. Ceram. Soc.* 2007. 90: 256.

13. Sirleto, L., Donato, M. G., Messina, G., Santangelo, S., Lipovskii, A. A., Tagantsev, D. K., Pelli, S. and Righini, G. C. Raman gain in niobium-phosphate glasses. *Appl. Phys. Lett.* 2009. 94: 031105.

14. Cole, J. M., Eck, E. R. H. V., Mountjoy, G., Anderson, R., Brennan, T., Wye, G.B., Newport, R.J. and Saunders, G.A. An x-ray diffraction and 31P MAS NMR study of rare-earth phosphate glasses, $(R_2O_3)_x$ $(P_2O_5)_{1-x}$, x= 0.175-0.263, R= La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er. *J. Phys.: Condens. Matter*. 2001. 13: 4105.

15. Struck, C. W. and Fonger, W. H. Role of the charge-transfer states in feeding and thermally emptying the ^5D states of Eu^{+3} in yttrium and lanthanum oxysulfides. *J. Lumin*. 1970. 1–2: 456.

16. Ivankov, A., Seekamp, J. and Bauhofer, W. Optical properties of Eu^{3+}-doped zinc borate glasses. *J. Lumin.* 2006. 121: 123.

17. Hache, F., Ricard, D., Flytzanis, C. and Kreibig. U. The optical kerr effect in small metal particles and metal colloids: The case of gold. *Appl. Phys. A: Mater. Sci. Process*. 1988. 47: 347.

18. Malta, O. L., Santa-Cruz, P. A., De Sá, G. F. and Auzel, F. Fluorescence enhancement induced by the presence of small silver particles in Eu^{3+}- doped materials. *J. Lumin*. 1985. 33: 261.

19. Chaumont, C. and Bernier, J. C. Superparamagnetism and magnetic granulometry of vitroceramics containing iron-lithium ferrite. *Solid State Commun*. 1983. 48: 357.

20. Falk, A. L., Koppens, F. H. L., Yu, V, Kang, K., Snapp, N. D. L., Akimov, A. V., Jo, M. H., Lukin, M. D. and Park, H. Near-field electrical detection of optical plasmons and single-plasmon sources. *Nat. Phys.* 2009. 5: 475.

21. Michaels, A. M., Nirmal, M. and Brus, L. E. Surface enhanced Raman spectroscopy of individual rhodamine 6G molecules on large Ag nanocrystals. *J. Am. Chem. Soc*. 1999. 121: 9932.
22. Kühn, S., Håkanson, U., Rogobete, L. and Sandoghdar, V. Enhancement of Single-Molecule Fluorescence Using a Gold Nanoparticle as an Optical Nanoantenna. *Phys. Rev. Lett.* 2006. 97: 017402.
23. Giri, N. K., Singh, A. K. and Rai, S. B. Efficient blue upconversion emission in Tm^{3+} via energy transfer from Yb^{3+} doped in lithium modified tellurite glass. *J. Appl. Phys.* 2007. 101: 033102.
24. Abd El-Ati, M. I. and Higazy, A. A. Electrical conductivity and optical properties of gamma-irradiated niobium phosphate glasses. *J. Mater. Sci*. 2000. 35: 6175.
25. Suratwala, T. I., Steele, R. A., Wilke, G. D., Campbell, J. H. and Takeuchi, K. Effects of OH content, water vapor pressure, and temperature on sub-critical crack growth in phosphate glass. *J. Non-Cryst. Solids.* 2000. 213: 263.
26. Liu, H. S., Chin,V. and Yung, S. W. FTIR and XPS studies of low-melting $PbO\text{-}ZnO\text{-}P_2O_2$ glasses. *J. Mater. Chem. Phys.* 1997. 50: 1.
27. Lakshmikantha, R., Rajaramakrishna, R., Anavekar, R. V. and Ayachit, N. H. Characterization and structural studies of lithium doped lead zinc phosphate glass system. *J. Mater. Chem. Phys*. 2012. 133: 249.
28. Martin, S. W. Review of the structures of phosphate glasses. *Eur. J. Solid State Inorg. Chem.* 1991. 28: 163.
29. Uchida, K., Kaneko, S., Omi, S., Hata, C., Tanji, H., Asahara, Y., Ikushima, A. J., Tokizaki, T. and Nakamura, A. Optical nonlinearities of a high concentration of small metal particles dispersed in glass: copper and silver particles. *J. Opt. Soc. Am. B.* 1994. 11: 1236.
30. Chaumont, C. and Bernier, J. C. Superparamagnetism and magnetic granulometry of vitroceramics containing iron-lithium ferrite. *Solid State Commun*. 1983. 48: 357.
31. Stookey, S. D. Coloration of glass by gold, silver, and copper. *J. Am. Ceram. Soc.* 1949. 32: 246.
32. Maurer, R. D. Nucleation and Growth in a Photosensitive Glass. *J. Appl. Phys.* 29: 1.

33. Matsuoka, J., Naruse, R., Nasu, H. and Kamiya, K. Preparation of gold microcrystal-doped oxide optical coatings through adsorption of tetrachloroaurate ions on gel films. *J. Non-Cryst. Solids.* 1997. 218: 151.
34. Tanahashi and Mitsuyu, T. Preparation and optical properties of silica gels in which small gold particles were grown by photoreduction, *J. Non-Cryst. Sol.* 1995. 181: 77-82.
35. Hai Lin, S. J., Wu, J., Song, F., Peyghambarian, N. and Pun, E. Y. B. Er^{3+} doped Na_2O–Nb_2O_5–TeO_2 glasses for optical waveguide laser and amplifier. *J. Phys. D: Appl. Phys.* 2003. 36: 812.
36. Scaffardi, L. B., Schinca, D. C. and Santillán, J. M. J. Quantitative optical extinction-based parametric method for sizing a single core–shell Ag–Ag_2O nanoparticle. *J. Phys. D: Appl. Phys.* 2011 44: 10510.
37. Fleischmann, M., Hendra, P. J. and McQuillan, A. J. Raman spectra of pyridine adsorbed at a silver electrode. *Chem. Phys. Lett.* 1974. 26: 163.
38. Weitz, D. A., Garoff, S., Gersten, J. I. and Nitzan, A. The enhancement of Raman scattering, resonance Raman scattering, and fluorescence from molecules adsorbed on a rough silver surface. *J. Chem. Phys.* 1983. 78: 5324.
39. Carmo, A. P., Anjos, V., de Almeida, R., da Silva, M. D. and Kassab, L. R. P. Thermo-optical properties of tellurite glasses doped with Eu^{3+} and Au nanoparticles. *J. Phys. D: Appl. Phys.* 2009. 42: 15540.
40. Snoeks, E., Lagendijk, A. and Polman, A. Measuring and Modifying the Spontaneous Emission Rate of Erbium near an Interface. *Phys. Rev. Lett.* 1995. 74: 2459.
41. Kumar, G. M., Rao, D. N. and Agarwal, G. S. Experimental studies of spontaneous emission from dopants in an absorbing dielectric. *Opt. Lett.* 2005. 30: 732.
42. Prasad, P. N. *Nanophotonics.* New York : Wiley. 2004.
43. Digonnet, M. J. *Rare Earth Doped Fiber Lasers and Amplifiers.* New York: Dekker. 1993.
44. Strohhofer, C. and Polman A. Silver as a sensitizer for erbium. *Appl. Phys. Lett.* 2002. 81: 1414.

45. Fu, G., Cai, W., Kan, C., Li, C. and Zhang, L. Controllable optical properties of Au/SiO nanocomposite induced by ultrasonic irradiation and thermal annealing. *Appl. Phys. Lett.* 2003. 83: 36.
46. Naranjo, L. P., de Araujo, C. B., Malta, O. L., Santa Cruz, P. A. and Kassab, L. R. P. Enhancement of Pr^{3+} luminescence in PbO–GeO_2 glasses containing silver nanoparticles. *Appl. Phys. Lett*. 2005. 87: 241914.
47. Mertens, H. and Polman, A. Plasmon-enhanced erbium luminescence. *Appl. Phys. Lett.* 2006. 89: 211107.
48. Hamanka, Y., Nakamura, A., Omi, S., Del Fatti, N., Vallee, F. and Flytzanis, C. Ultrafast response of nonlinear refractive index of silver nanocrystals embedded in glass. *Appl. Phys. Lett.* 1999. 75: 1712.
49. Qu, S., Zhao, C., Jiang, X., Fang, G., Gao, Y., Zeng, H., Song, Y., Qiu, J. Zhu, C. and Hirao, K. Optical nonlinearities of space selectively precipitated Au nanoparticles inside glasses. *Chem. Phys. Lett.* 2003. 368: 352.
50. Yamane, M. and Asahara, Y. *Glasses for Photonics*. Cambridge: Cambridge University Press. 2000.
51. Flytzanis, C., Hache, F., Klein, M. C. and Ricard, D. *Progress in optics XXIX*. Amsterdam: Elsevier Sciences. 1991.
52. Hayakawa, T., Selvan, S. and Nogami, M. Remarkable influence of silver islands on the enhancement of fluorescence from Eu^{3+} ion-doped silica gels. *Appl. Phys. Lett*. 1999. 74: 1513.
53. Abd El-Ati, M. I. and Higazy, A. A. Electrical conductivity and optical properties of gamma-irradiated niobium phosphate glasses. *J. Mater. Sci.* 2000. 35: 6175.
54. Suratwala, T. I., Steele, R. A., Wilke, G. D., Campbell, J. H. and Takeuchi, K. Effects of OH content, water vapor pressure, and temperature on sub-critical crack growth in phosphate glass. *J. Non-Cryst. Solids.* 2000. 213: 263.
55. de Camargo, A. S. S. Energy transfer processes in Yb^{3+}–Tm^{3+} co-doped sodium alumino-phosphate glasses with improved 1.8 µm emission. *J. Phys.: Condens. Matter*. 2008. 20: 255240.
56. Kumar, G. M., Rao, D. N. and Agarwal, G. S. Measurement of Local Field Effects of the Host on the Lifetimes of Embedded Emitters. *Phys. Rev. Lett.* 2003. 91: 203903.

57. Mattarelli, M., Montagna, M., Vishnubhatla, K., Chiasera, A., Ferrari, M. and Righini, G. C. Mechanisms of Ag to Er energy transfer in silicate glasses: A photoluminescence study. *Phys. Rev. B.* 2007. 75: 125102.

58. de Almeida, R., daSilva, D. M., Kassab, L. R. P. and de Araujo, C. B. Eu3+ luminescence in tellurite glasses with gold nanostructures. *Opt.Commun.* 2008. 281: 108.

59. Carmo, A. P., Bell, J. V., Anjos, V., de Almeida, R., da Silva, D. M. and Kassab, L. R. P. Thermo-optical properties of tellurite glasses doped with Eu^{3+} and Au nanoparticles. *J. Phys. D: Appl. Phys.* 2009. 42: 155404.

60. Malta, O. L., Santa-Cruz, P. A., De Sá, G. F. and Auzel, F. Fluorescence enhancement induced by the presence of small silver particles in Eu^{3+}- doped materials. *J. Lumin.* 1985. 33: 261.

61. El-Mallawany, R.A.H. *Tellurite glasses handbook-physical properties and data.* Florida:Taylor and Francis. 2010.

62. Souza Neto, N.M., Ramos, A.Y. and Barbosa, L.C. Er^{3+}environment in TeO_2–ZnO–Na_2O glasses. *J. Non. Crys. Solids.* 2002. 304: 195.

63. Jha, A., Shen, S. and Naftaly, M. Structural origin of spectral broadening of 1.5-μm emission in Er^{3+}-doped tellurite glasses. *Phys. Rev. B.* 2000. 62: 6215.

64. Auzel, F., Bonfigli, F., Gagliari, S. and Baldacchini, G. The interplay of self-trapping and self-quenching for resonant transitions in solids; role of a cavity. *J. Lumin.* 2001. 94: 293.

65. Ravi Kanth Kumar, V. V., George, A.K., Knight, J.C. and Russell, P.S.J. Tellurite photonic crystal fiber. *Opt. Exp.* 2003. 11: 2641.

66. Tanabe, S. Fluorescence properties of Er^{3+} ions in glass ceramics containing LaF_3 nanocrystals. *Opt. Mater.* 2002. 19: 343.

67. Vijaya Prakash, G., Narayana Rao, D. and Bhatnagar, A. K. Linear optical properties of niobium-based tellurite glasses. *Solid State Commun.* 2001. 119: 39.

68. Mori, A., Ohishi, Y. and Sudo, S. Erbium-doped tellurite glass fibre laser and amplifier. *Elect. Lett.* 2002. 33:863.

69. Inoue, S., Nukui, A., Yamamoto, K., Yano, T., Shibata, S. and Yamane, M. Refractive index patterning of tellurite glass surfaces by ultra short pulse laser spot heating. *J. Mater. Sci.* 2002. 37: 3459.

70. Chillcce, E. F., Rodriguez, E., Neves, A. A. R., Moreira, W. C., Ce´sar, C. L. and Barbosa, L. C., Er^{3+}–Tm^{3+} co-doped tellurite fibers for broadband optical fiber amplifier around 1550 nm band. *Opt. Fiber Tech*. 2006. 12: 185.

71. Huang, L., Jha, A., Shen, S. and Chung, W.J. Visible emissions at 592 and 613 nm in Er^{3+}–Eu^{3+}-codoped tellurite fibers. *Opt. Commun*. 2004. 239: 403.

72. Chen, D. Intense ultraviolet upconversion luminescence from Tm3+/Yb3+: β-YF3 nanocrystals embedded glass ceramic. *J. Appl. Phys*. 2007. 101: 113511.

73. Kishi, Y. Fabrication and Efficient Infrared-to-Visible Upconversion in Transparent Glass Ceramics of Er–Yb Co-Doped CaF_2 Nano-Crystals. *J. Am. Ceram. Soc*. 2005. 88: 3423.

74. Liu, Y.H. Energy transfer in Yb^{3+}-Er^{3+}-codoped bismuth borate glasses. *J. Opt. Soc. Am. B*. 2007. 24: 1046.

75. Sahar, M. R., Sulhadi, K. and Rohani, M. S. Spectroscopic studies of TeO_2–ZnO–Er_2O_3 glass system. *J. Mater. Sci*. 2007. 42: 824.

76. Sahar, M.R., Sulhadi, K. and Rohani. M. S. The preparation and structural studies in the $(80 - x)TeO_2$–20ZnO–$(x)Er_2O_3$ glass system. *J. Non-Cryst. Solids*. 2008. 354: 1179.

77. El-Hagary, M., Emam-Ismail, M., Shaaban, E.R. and Shaltout, I. Optical properties of glasses (TeO_2–GeO_2–K_2O) thin films co-doped with rare earth oxides Sm_2O_3/Yb_2O_3. *J. Alloys Compd*. 2009. 485: 519.

78. Xiao, K. and Yang, Z. Thermal stability and optical transitions of Er^{3+}/Yb^{3+}-codoped barium gallogermanate glass. *Opt. Mater*. 2007. 29: 1475.

79. Sidek, H. A. A., Rosmawati, S., Talib, Z. A., Halimah, M. K. and Daud, W. M. Synthesis and optical properties of ZnO-TeO_2 glass system. *Amer. J. Appl. Sc*. 2009. 6: 1489.

80. Babu, P., Seo, H. J., Kesavulu, C. R., Jang, K. H. and Jayasankar, C. K. Thermal and optical properties of Er^{3+}-doped oxyfluorotellurite glasses. *J. Lumin*. 2009. 129: 444.

81. Yang, Y., Yang, Z., Chen, B., Li, P., Li, X. and Guo, Q. Spectroscopic properties and thermal stability of Er3+-doped germanate–borate glasses. *J. Alloys Compd*. 2009. 479: 883.

82. Shen, X., Nie, Q.H., Xu, T.F., Dai, S.X., Li, G.P. and Wang, X.S. Effect of Ce^{3+} on the spectroscopic properties in Er^{3+} doped TeO_2–GeO_2–Nb_2O_5–Li_2O glasses. 2007. *J. Lumin.* 126: 273.
83. Chen, F., Xu, T., Dai, S., Nie, Q., Shen, X., Zhang, J. and Wang, X. Linear and non-linear characteristics of tellurite glasses within TeO_2–Bi_2O_3–TiO_2 ternary system. *Opt. Mater.* 2010. 32: 868.
84. Jlassi, I., Elhouichet, H., Ferid, M. and Barthou, C. Study of photoluminescence quenching in Er^{3+}-doped tellurite glasses. *Opt Mater*. 2010. 32: 743.
85. Zhao, Z., Jia, T., Lin, J., Wang, Z. and Sun, Z. Femtosecond non-resonant optical nonlinearity of silver chloride nanocrystal doped niobic tellurite glass. *J. Phys. D: Appl. Phys.* 2009 42: 045107.
86. Madden, S. J. and Vu, K. T. Very low loss reactively ion etched Tellurium Dioxide planar rib waveguides for linear and non-linearoptics. *Opt Express.* 2009. 17: 17645.
87. Lin, H., Meredith, G., Jiang, S., Peng, X., Luo, T., Peyghambarian, N. and Pun, E.Y.B. Optical transitions and visible upconversion in Er^{3+} doped niobic tellurite glass. *J. Appl. Phys.* 2003 93: 186.
88. Lin, J., Huang, W. H., Sun, Z. R., Ray, C. S. and Day, D. E. Structure and non-linear optical performance of TeO_2–Nb_2O_5–ZnO glasses. *J. Non-Cryst. Solid*. 2005. 336: 189.
89. Mirgorodsky, A.P., Soulis, M., Thomas, P., Merle-Mjean, T. and Smirnov, M. Ab initio study of the nonlinear optical susceptibility of TeO_2-based glasses. *Phys. Rev. B*. 2006. 73: 134206.
90. Rai, V.K. and Rai, S.B. A comparative study of FIR and FL based temperature sensing schemes: an example of Pr^{3+}. *Appl. Phys. B*. 2007. 87: 323.
91. Lin, J., Huang, W., Li, B., Jin, C., Liu, C., Lei, S. and Sun, Z. Preparation of AgCl Nano-Crystal Embedded Tellurite Nonlinear Optical Glasses under Electric Field Accompanied Heat Treatment. *J. Mater. Sci. Technol.* 2008. 24: 863.
92. Eroni, P. dos Santos. F., Fávero, F. C., Gomes, A. S. L., Xing, J., Chen, Q., Fokine, M. and Carvalho, I. C. S. Evaluation of the third-order nonlinear

optical properties of tellurite glasses by thermally managed eclipse Z-scan. *J. Appl. Phys.* 2009. 105: 024512.

93. Amjad, R. J., Sahar, M. R., Ghoshal, S. K., Dousti, M. R., Riaz, S., Samavati, A. R., Jamaludin, M. N. A. and Naseem, S. Plasmon Enhanced Upconversion Fluorescence in Er^{3+}:Ag Phosphate Glass: Effect of Heat Treatment. *Chin. Phys. lett.* 2013. 30: 027301.
94. Kassab, L. R. P., de Almeida, R., da Silva, D. M., de Assumpção, T. A. A. and de Araújo, C. B. Enhanced luminescence of Tb/Eu doped tellurium oxide glass containing silver nanostructures. *J. Appl. Phys.* 2009. 105: 103505.
95. Kassab, L. R. P., de Almeida, R., da Silva, D. M. and de Araújo, C. B. Luminescence of Tb^{3+} doped TeO_2–ZnO–Na_2O–PbO glasses containing silver nanoparticles. *J. Appl. Phys.* 2008. 104: 093531.
96. Singh, S.K., Giri, N.K., Rai, D.K. and Rai, S.B. Enhanced upconversion emission in Er $^{3+}$-doped tellurite glass containing silver nanoparticles. *Sol State Sci*. 2010. 12: 1480.
97. Mizuno, S., Benino, Y., Fujiwara, T. and Komatsu, T. Selected Topics in Applied Physics LA eng TE Solid Photonic Bandgap Fibres and Applications. *Jap. J. Appl. Phys.* 2006. 45: 6121.
98. Ueda, J., Tanabe, S. and Ishida, A. Surface plasmon excited infrared-to-visible upconversion in Er^{3+}-doped transparent glass ceramics. *J. Non-Crystal. Sol.* 2009. 355: 1912.
99. Jiang, L., Sun, Z. R., Zhu, X. R., Zeng, H. P., Xu, Z.Z., Wang, Z. G., Lin, J., Huang, W. H., Armstrong, R. S. and Lay, P. A. Optical bistability for ZnO–Nb_2O_5–TeO_2 glasses. *Opt. Mater.* 2004. 25: 401.
100. Tikhomirov, V. K., Drisen, K., Walrand, C. G. and Mortier, M. Broadband telecommunication wavelength emission in Yb^{3+}-Er^{3+}-Tm^{3+} co-doped nano-glassceramics. *Opt. Exp.* 2007. 15: 9535.
101. Suyver, J. F. , Grimm, J., van Veen, M. K., Biner, D., Krämer, K. W. and Güdel, H. U. Upconversion spectroscopy and properties of $NaYF_4$ doped with Er^{3+}, Tm^{3+} and/or Yb^{3+}. *J. Lumin.* 2006. 117: 1.
102. Kassab, L. R. P., de Araújo Cid, B., Kobayashi, R.A., de Almeida, P. R. and da Silva, D.M. Influence of silver nanoparticles in the luminescence efficiency of Pr-doped tellurite glasses. *J. Appl. Phys.* 2007. 102: 103515.

103. Lin, J., Huang, Lei, S. H., Liu, C. C., Bian, Q., Ma, L. N. and Li, D. W. Preparation of silver nano-crystal patterns patterns in oxide glasses under electric field accompanied by heat treatment. *J. Cer. Proc. Res.* 2008. 9: 416.

104. Balaji, S., Misra, D. and Debnath, R. Enhanced Green Emission from Er2WO6 Nanocrystals Embedded Composite Tellurite Glasses. *J. Fluoresc*. 2011. 10: 895.

105. Mustafa, B. Solar Technological Progress and Use of Solar Energy in the World. *Eng. Sources Part A: Recover. Util. Env. Eff.* 2006. 28: 10.

106. Švrček, V., Slaoui, A. and Muller, J. C. Silicon Nanocrystals as Light Converter for Solar Cells. *Thin Sol Films*. 2004. 451-452: 388.

107. James, P. Legal Fights May Follow More Sun Energy Use. *J. Am. Bar Assoc*. 1991. 67: 544.

108. Peter, M. *Solar Projects Draw New Opposition (The Business of Green)*. New York Times:New York. 24 September 2008.

109. Fan, X., Chu, Z., Chen, L., Zhang, C., Wang, F., Tang, Y., Sun, J. and Zou, D. Fibrous flexible solid-type dye-sensitized solar cells without transparent conducting oxide. *Appl. Phys. Lett.* 2008. 92: 113510.

110. Ramier, J., Plummer, C., Leterrier, Y., Manson, J., Eckert, B. and Gaudiana, R. Mechanical integrity of dye-sensitized photovoltaic fibers. *Renew Energy.* 2008. 33: 314.

111. Liu, J., Namboothiry, M. and Carroll, D. Fiber-based architectures for organic photovoltaics. *Appl. Phys. Lett.* 2007. 90: 063501.

112. O’Connor, B., Pipe, K. and Shtein, M. Fiber based organic photovoltaic devices. *Appl. Phys. Lett.* 2006. 92: 193306.

113. Dennler, G., Scharber, M., Ameri, T., Denk, P., Forberich, K., Waldauf, C. and Brabec, C. Design Rules for Donors in Bulk-Heterojunction Tandem Solar Cells Towards 15% Energy-Conversion Efficiency. *Adv. Mater.* 2008. 20: 579.

114. Chandra, S. Super Ionic Solids Principles and Applications. Holland: North Holland Publishing Company. 1981.

115. Meggers, F.W. Atomic Spectra of Rare Earth Elements. *Rev. Mod. Phys.* (1942) 14: 96.

116. Wybourne, B. G., The fascination of the rare earths—then, now and in the future, *J. Alloys Compd*. (2004) 96: 380.
117. Van Vleck, J.H., Frank, A. The Effect of Second Order Zeeman Terms on Magnetic Susceptibilities in the Rare Earth and Iron Groups, *Phys. Rev.* (1929) 34: 1494.
118. Van Vleck, J.H. Theory of Electric and Magnetic Susceptibilities, Oxford Universty Press. 1932.
119. Penney, W.G., Schlapp, R. The Influence of Crystalline Fields on the Susceptibilities of Salts of Paramagnetic Ions. I. The Rare Earths, Especially Pr and Nd. *Phys. Rev.* (1932) 41: 194.
120. Frank, A. Temperature Variation of the Magnetic Susceptibility, Gyromagnetic Ratio, and Heat Capacity in Sm^{+++} and Eu^{+++} *Phys. Rev.* (1932) 39 :119.
121. Frank. A. The Effect of Crystalline Fields on the Magnetic Susceptibilities of Sm^{+++} and Eu^{+++}, and the Heat Capacity of Sm^{+++} *Phys. Rev.* (1935) 48: 765.
122. Judd, B. R. Optical absorption intensities of rare-earth ions. *Phys. Rev.* 1962. 127: 750.
123. Ofelt, G. S. Intensities of Crystal Spectra of Rare-Earth Ions. *J. Chem. Phys.* 1962. 37: 511.
124. Griffith, J.S. Some investigations in the theory of open-shell ions *Mol. Phys.* (1960) 3: 477.
125. Carnall, W. T., Fields, P. R. and Rajnak, K. Spectral Intensities of the Trivalent Lanthanides and Actinides in Solution. II. Pm, Sm, Eu, Gd, Tb, Dy, and Ho. *J. Chem. Phys.* 1968. 49: 4450.
126. Maier, S. A. Plasmonics: Fundamentals and Applications, US: Springer. (2007).
127. Robert, B. W. Nonlinear Optics. San Diego: Academic Press. 2003.
128. Karmakar, B., Som, T., Singh,S. P., and Nath, M.,Nanometal-Glass Hybrid Nanocomposites: Synthesis, Properties and Applications. *Trans. Ind. Ceram. Soc.*, 2010. 69: 171.
129. John, D. J. Classical Electrodynamics. New York: John Wiley & Sons. 1999.

130. Som, T. and Karmakar. B. Nephelauxetic effect of low phonon antimony oxide glass in absorption and photoluminescence of rare-earth ions. *Spectrochim Actat A*. 2011. 79: 1766.

131. Urbach, F. The long-wavelength edge of photographic sensitivity and of the electronic absorption of solids. *Phys. Rev*. 1953. 92: 1324.

132. Davis, E. A. and Mott, N. F. Conduction in non-crystalline system V. Conductivity, optical absorption and photoconductivity in amorphous semiconductors. *Philos. Mag*. 1970. 22: 0903.

133. Al.-Ani, S. K. J. and Higazy. A. A. Study of optical absorption edges in $MgO-P_2O_5$ glasses. *J. Mater. Sci.* 1991. 26: 3670.

134. Hassan, M. A. and Hogarth, C. A. A comparison of the optical properties of glass and of evaporated amorphous thin films of $BaO-TeO_2$. *J. Mater. Sci*. 1988. 23: 2500.

135. Dayanand, C., Bhikshamaiah, G. and Salagram, M. IR and optical properties of PbO glass containing a small amount of silica. *Mater. Lett*. 1995. 23: 309.

136. Chopra, K. L. and Bahl, S. K. Exponential tail of the optical absorption edge of amorphous semiconductors. *Thin Sol. Films*. 1972. 11: 377.

137. Pátek, K. *Glass Lasers*. London: Butterworth. 1970.

138. Dragan, A.I., Bishop, E.S.,Casas-Finet, J.R., Strouse, R.J., McGivney, J.,Schenerman, M.A. and Geddes, C.D. Distance Dependence of Metal-Enhanced Fluorescence. *Plasmon*. 2012. 7: 739.

139. Aye, N. N. Study of xP_2O_5-(1-x-y)V_2O_5-yCuO Semi-conducting Glass System *Univ. Res. Jour.* 4: 39 (2011).

140. Liu, C. and Heo, J. Local Heating from Silver Nanoparticles and Its Effect on the Er^{3+} Upconversion in Oxyfluoride Glasses. *J. Amer. Ceram. Soc*. 2010. 93: 3349.

141. Al.-Ani, S. K. J. and Higazy, A. A. Study of optical absorption edges in $MgO-P_2O_5$ glasses. *J. Mater. Sci.* 1991. 26: 3670.

142. Malta, O. L. and Couto dos Santos, M. A. Theoretical analysis of the fluorescence yield of rare earth ions in glasses containing small metallic particles. *Chem. Phys. Lett.* 1990. 174: 13.

143. Selvan, S. T., Hayakawa, T. and Nogami, M. Remarkable influence of silver islands on the enhancement of fluorescence from Eu^{3+} ion-doped silica gels. *J. Phys. Chem. B.* 1999. 103: 7064.

144. Strohhöfer, C. and Polman, A. Silver as a sensitizer for erbium. *Appl. Phys. Lett.* 2002. 81: 1414.

145. Barnes, W. L., Dereux, A. and Ebbesen, T. W. Surface plasmon subwavelength optics. *Nature (London)*, 2003. 424: 824.

146. Geddes, C. D. and Lakowicz, J. R. metal enhanced fluorescence solution-based sensing platform. *J. Fluorosc.* 2002. 12: 121.

147. Lakowicz, J. R. Radiative decay engineering: biophysical and biomedical applications. *Anal, Biochem.* 2001. 298: 1.

148. Bouhelier, A. Field-enhanced scanning near-field optical microscopy. *Microsc. Res. Tech*. 2006. 69: 563.

149. Bomfim, F. A., Martinelli, J. R., Kassab, L. R. P., Assumpção, T. A. A. and de Araújo, C. B. Infrared-to-visible upconversion in Yb^{3+}/Er^{3+} co-doped PbO–GeO_2glass with silver nanoparticles. *J. Non-Cryst. Sol.* 2010 356: 2598.

150. Le Saoût, G., Simon, P., Fayon, F., Blin, A. and Vaills, Y. Raman and infrared study of $(PbO)_x(P2O5)_{(1-x)}$ glasses. *J. Raman Spectrosc*. 2002. 33: 740.

151. Hafid, M., Jermoumi, T., Niegisch, N. and Mennig, M. Thermal and infrared characterization of new barium-iron-metaphosphate glasses. *Mat. Res. Bullet*. 2001. 36: 2375.

152. Reis, S.T., Faria, D.L.A., Martinelli, J.R., Pontuschka, W.M., Day, D.E. and Partiti, C.S.M. Structural features of lead iron phosphate glasses. *J. Non-Cryst. Solids*. 2002. 304: 188.

153. Ilieva, D., Jivov, B., Bogachev, G., Petkov, C., Penkov, I. and Dimitriev, Y. Infrared and Raman spectra of Ga_2O_3–P_2O_5 glasses. *J. Non-Cryst. Solids*. 2001. 283: 195.

154. Dayanand, G.B.C, Tyagaraju, V. J., Salagram, M. and Murthy, A. S. R. Structural investigations of phosphate glasses: a detailed infared study of the x(PbO)-(1-x)P_2O_5 vitreous system, *J. Mat. Sci.* 1996. 31: 1945.

155. Awang, A., Ghoshal. S.K. Sahar. M.R., Dousti, M. R., Amjad, R. J., Nawaz, F., Enhanced spectroscopic properties and Judd-Ofelt parameters of Er-doped

tellurite glass: Effect of gold nanoparticles. *Curr. Appl. Phys.* http://dx.doi.org/10.1016/j.cap.2013.06.025.

156. Khor, S. F., Talib, Z. A. and Mat Yunus, W. M. Optical properties of ternary zinc magnesium phosphate glasses. *Ceram. Int.* 2012. 38: 935.
157. Talib, Z. A., Daud, W. M., Tarmizi, E. Z. M., Sidek, H. A. A. and Yunus, W. M. M. Optical absorption spectrum of Cu_2O–CaO–P_2O_5 glasses. *J. Phys. Chem. Sol.* 2008. 69: 1969.
158. Elechiguerra, J. L., Reyes-Gasga, J. and Yacaman, M. J. The role of twinning in shape evolution of anisotropic noble metal nanostructures. *J. Mater. Chem.* 2006. 16: 3906.
159. Wei, Q. H., Su, K. H., Zhang, X., Mock, J. J., Smith, D. R. and Schultz, S. Interparticle coupling effects on plasmon resonances of nanogold particles. *Nano lett.* 2003. 3: 1087.
160. Ghoshal, S. K., Sahar, M. R., Rohani, M. S. and Sharma, S. Temperature dependent luminescence in erbium-doped zinc tellurite glass: A model investigation. *Indian J. Pure. Ap. Phy.* 2011. 49: 509.
161. Ghoshal, S. K., Sahar, M. R., Dousti, M. R., Sharma, S., Rohani, M. S., Arifin, R. and Hamzah, K. Model for up-conversion luminescence in silver nanoparticles embedded erbium-doped tellurite glass. *Indian J. Pure. Ap. Phy.* 2012. 50: 555.
162. Som, T. and Karmakar, B. Nanosilver enhanced upconversion fluorescence of erbium ions in Er^{3+}: Ag-antimony glass nanocomposites. *J. Appl. Phys.* 2009. 105: 013102.
163. Bonner, Jr. C. E., Mwangi, P. M., Creekmore, S. J., Richardson, L. J., Stefanos, S. and Loutts, G. B. A spectroscopic and Judd–Ofelt analysis of the relaxation dynamics of Tm3+ in the fluorapatites, FAP, S-FAP, and B-FAP. *Opt. Mater.* 2002. 20: 1.
164. Sardar, D. K., Gruber, J. B., Zandi, B., Hutchinson, J. A. and Trussell, C. W. Judd–Ofelt analysis of the $Er^{3+}(4f^{11})$ absorption intensities in phosphate glass: Er^{3+}, Yb^{3+}. *J. Appl. Phys.* 2003. 93: 2041.
165. Babu, P., Seo, H. J., Jang, K. H., Balakrishnaiah, R., Jayasankar, C. K., Lim, K. S. and Lavin, V. Optical spectroscopy, 1.5 μm emission, and upconversion

properties of Er^{3+}-doped metaphosphate laser glasses. *J. Opt. Soc. Am. B.* 2007. 24: 2218.

166. Xia, H., Lin, Q., Zhang, J. and Zhang, Q. 2 μm mid-infrared optical spectra of Tm3+-doped germanium gallate glasses. *J. Rare Earth*. 2009. 27: 781.
167. Walsh, B. M., Barnes, N. P., Reichle, D. J. and Jiang. S. Optical properties of Tm3+ions in alkali germanate glass. *J. Non-Cryst. Sol.* 2006. 352: 5344.
168. Kassab, L. P. R., Ferreira Freitas, L., Ozga, K. and Brik, M. G., Wojciechowski. A., ZnO–TeO_2–Yb/Tm glasses with silver nanoparticles as laser operated quantum electronic devices. *Opt. Laser Technol.* 2010. 42: 1340.
169. Yu, S., Yang, Z. and Xu, S. Judd–Ofelt and laser parameterization of Tm^{3+}-doped barium gallo-germanate glass fabricated with efficient dehydration methods. *Opt. Mater.* 2009. 31: 1723.
170. Bolschikov, F. A., Kuz'micheva, G. M., Lis, D. A., Papin, Yu. M., Popov, A. V. and Ryabochkina, P. A. Growth, refined structural and spectroscopic characteristics of Tm^{3+}-doped $NaGd(WO_4)_2$ single crystals. *J. Cryst. Growth*. 2009. 311: 4171.
171. Zhang, L. Z., Wang, G. F. and Lin, S. K. Synthesis, growth and spectral properties of Tm^{3+}/Yb^{3+}-codoped YVO_4 crystal. *J. Cryst. Growth*. 2002. 241: 325.
172. Lakshman, S. V. J. and Kumar. A. S. Optical absorption spectra of Pr (III), Nd (III), Er (III) and Tm (III) ions in potassium sodium phosphate glass. *J. Phys. Chem. Sol.* 1988. 49: 133.
173. Bao-Quan, Y., Liang-Liang, Z., Xiao-Ming, D., Guang-Jun, Z. and Yan-Hua, Z. Judd–Ofelt analysis of spectra and experimental evaluation of laser performance of Tm^{3+} doped Lu_2SiO_5 crystal. *Chin. Phys. B.* 2008. 17: 3635 (2008).
174. Silvestre, O., Pujol, M. C., Rico,V., Guell,V., Aguilo, M. and Diaz, F. Thulium doped monoclinic KLu $(WO_4)_2$ single crystals: growth and spectroscopy. *Appl. Phys. B.* 2007. 87: 707.
175. Yanmin, Baoquan, Y., Baojiu, C., Cheng, W., Guozhong, R. and Xiaojun, W. Judd–Ofelt analysis of spectroscopic properties of Tm^{3+}, Ho^{3+} doped $GdVO_4$ crystals. *Opt. Mater.* 2007. 29: 1159.

176. Yanling, L., Yongbing, D., Jun, W., Yang, Y., Anping, D. and Shenghua, L. Spectra and intensity parameters of Tm^{3+} ion in $YAlO_3$ crystal. *Opt. Comm*. 2007. 273: 182.

177. Xiuai, L., Zhenyu, Y., Jianfu, L., Zhaojie, Z., Guohua, J. and Baichang, W. Optical spectra of Tm^{3+} doped $NaBi(WO_4)_2$. *Opt. Mater.* 2007. 29: 849.

178. Wei, Y., Tu, C., Wang, H., Yang, F., Jia, G. and You, Z. Thermal and optical properties of Tm^{3+}: NaLa $(WO_4)_2$ crystal. *Appl. Phys. B*. 2007. 86: 529.

179. Troshin, A. E., Kisel, V. E., Kuleshov, N. V., Pavlyuk, A. A. and Dunina, E. B. Spectroscopy and laser properties of Tm^{3+}: KY $(WO_4)_2$ crystal. *Appl. Phys. B*. 2007. 86: 287.

180. Reddy, A. A., Babu, S.S., Pradeesh, K., Otton, C.J. and Vijaya, P. G. Optical properties of highly Er^{3+}-doped sodium–aluminium–phosphate glasses for broadband 1.5µm emission. *J. Alloys Compd*. 2011. 509: 4047.

181. Matveeva, E. G., Shtoyko, T., Gryczynski, I., Akopova, I. and Gryczynski, Z. Fluorescence quenching/enhancement surface assays: Signal manipulation using silver-coated gold nanoparticles. *Chem. Phys. Lett.* 2008. 454: 85.

182. Pribik, R., Dragan, A.I., Zhang, Y., Gaydos, C. and Geddes, C.D. Metal-Enhanced Fluorescence (MEF): Physical characterization of Silver-island films and exploring sample geometries. *Chem. Phys. Lett*. 2009. 478: 70.

183. Enderlein. Single-molecule fluorescence near a metal layer. *J. Chem. Phys*.1999. 247: 1.

184. Amjad, R. J., Sahar, M.R., Ghoshal, S.K., Dousti, M.R., Riaz, S., Samavati, A.R., Arifin, R. and Naseem, S. Enhanced infrared to visible upconversion emission in Er^{3+}doped phosphate glass: Role of silver nanoparticles. *J. Lumin*. 2013. 136: 145.

185. Chiasera, A., Ferrari, M., Mattarelli, M., Montagna, M., Pell, S., Portales, H., Zheng, J. and Righini, G. C. Assessment of spectroscopic properties of erbium ions in a soda-lime silicate glass after silver–sodium exchange. *Opt. Mater*. 2005. 27: 1743.

186. Mattarelli, M., Montagna, M., Vishnubhatla, K., Chiasera, A., Ferrari, M. and Righini, G. C. Mechanisms of Ag to Er energy transfer in silicate glasses: A photoluminescence study. *Phys. Rev. B*. 2007. 75: 125102 .

187. Portales, H., Mattarelli, M., Montagna, M., Chiasera, A., Ferrari, M., Martucci, A., Mazzoldi, P., Pelli, S. and Righini, G. C., Investigation of the role of silver on spectroscopic features of Er^{3+}-activated Ag-exchanged silicate and phosphate glasses. *J. Non-Cryst.Sol*. 2005.351:1738.

188. Mattarelli, M., Montagna, M., Moser, E., Vishnubhatla, K. C., Armellini, C., Chiasera, A., Ferrari, M., Speranza, G., Brenci, M., Nunzi, C. G. and Righini, G. C. Silver to erbium energy transfer in phosphate glasses. *J. Non-Cryst. Sol*. 2007. 353: 498.