STUDIES ON THE LINEAR AND NONLINEAR OPTICAL BEHAVIOUR OF COLLOIDAL METALLIC AND METALLOID NANOSTRUCTURES

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by

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To my teachers

and

my family

CERTIFICATE

This is to certify that the thesis entitled, *"**Studies on the linear and nonlinear optical behaviour of colloidal metallic and metalloid nanostructures"*** being submitted by ***Priyadarshini M,*** to the Indian Institute of Technology Delhi, New Delhi, for the award of degree of ***Doctor of Philosophy*** in Physics is a record of Bonafede research work carried out by her under my supervision and guidance. She has fulfilled the requirements for submission of the thesis, which to the best of my knowledge has reached the requisite standard.

The material contained in the thesis has not been submitted in part or full to any other University or Institute for the award of any degree or diploma.

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ABSTRACT

The present thesis is a comprehensive and elaborate relativistic study on metal (Au) and metalloid (Ge) nano-colloids fabricated from two diverse methods- femtosecond laser ablation and chemical synthesis. The study broadly aims to understand their relative femtosecond laser based optical nonlinearities and ultrafast absorption dynamics behaviour based on differences in their fabrication methodologies. This systematic study reveals significant difference in the optical nonlinearities (nonlinear absorption and nonlinear refractive index) observed when the nano-colloids experience intense femtosecond laser pulses. Furthermore, the thesis establishes a clear understanding of the higher order nonlinearities (induced by many photon interactions), the excited state saturation and reverse saturation of absorption and so on. The dynamic evolution of absorption of nano-colloids while co-pumped with an intense femtosecond laser pulse reveal many interesting aspects pertaining to ground-state electron population or depopulation/bleaching and photo induced excited state absorption phenomena. All these specific and targeted studies are of potential use in many diverse optoelectronic, biphotonic and medical photonic applications. Broadly, the presented study serves as an extremely useful tool to decide the appropriate colloidal metal/metalloid nanoparticle synthesis method for wide varieties of nonlinear optics-based applications, based on the selective choice of fabrication and material specific protocols.

एब्स्ट्रैक्ट

वर्तमान थीसिस धातु (गोल्ड) और मेटलॉइड (जर्मेनियम) नैनो-कोलाइड्स पर एक व्यापक और विस्तृत रिलेटिविस्टिक अध्ययन है जो दो विविध विधियों- फेमटोसेकंड लेजर एब्लेशन और रासायनिक संश्लेषण से निर्मित है। अध्ययन का विस्तृत उद्देश्य उनके निर्माण के तरीकों में अंतर के आधार पर उनके सापेक्ष फेमटोसेकंड लेजर आधारित ऑप्टिकल नॉन लीनियरटी और अल्ट्राफास्ट अवशोषण गतिकी व्यवहार को समझना है। यह व्यवस्थित अध्ययन बताता है कि जब नैनो-कोलॉइड तीव्र फेम्टोसेकंड लेजर पल्सेस का सामना करते हैं तब ऑप्टिकल नॉन लीनियरटी (नॉनलीनियर अवशोषण और नॉनलीनियर रिफ्रैक्टिव इंडेक्स) में महत्वपूर्ण अंतर होता है। इसके अलावा, थीसिस उच्च क्रम की नॉन लीनियरटीस (मल्टी फोटॉन इंटरैक्शन से प्रेरित), एक्साइटेड स्टेट सेचुरेशन और रिवर्स सेचुरेशन ऑफ़ एब्सॉर्प्शन आदि की स्पष्ट समझ प्रदान करती है। नैनो-कोलॉइड के अवशोषण का गतिशील विकास, एक तीव्र फेम्टोसेकंड लेजर पल्स के साथ सह-पंप करते समय ग्राउंड स्टेट इलेक्ट्रान पापुलेशन या डि-पॉपुलेशन / ब्लीचिंग और फोटो उत्तेजित स्थिति संवेदन घटनाओं से संबंधित कई रोचक पहलू उजागर करता है । ये सभी विशिष्ट और निर्दिष्ट अध्ययन विभिन्न विविध ऑप्टोइलेक्ट्रॉनिक, बाइफोटोनिक और चिकित्सा फोटोनिक अनुप्रयोगों में अत्याधिक उपयोगी होते हैं । मोटे तौर पर, प्रस्तुत अध्ययन निर्माण और सामग्री विशिष्ट प्रोटोकॉल के चयनात्मक विकल्प के आधार पर, नॉनलीनियर प्रकाशिकी-आधारित अनुप्रयोगों की विस्तृत किस्मों के लिए उपयुक्त कोलाइडल धातु/मेटलॉइड नैनोपार्टिकल संश्लेषण विधि तय करने के लिए एक अत्यंत उपयोगी उपकरण के रूप में कार्य करता है।

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Figure 6.6: Laser intensity dependent (a) Open aperture (OA) and (b) Closed aperture (CA) Z-scan of Ge NPs colloid at 800 nm. Intensity dependent variation of (c) three-photon absorption (3PA) coefficient (γ) and (d) nonlinear refraction inducing phase shift $(\Delta\phi)_{NR}$, (e) nonlinear absorption inducing phase shift $(\Delta\varphi)_{NA}$ and (f) nonlinear refractive index (n_2) extracted from Fig. 5a and Fig. 5b respectively. (λ=800 nm, 120 fs, 1 kHz).

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Abbreviations

XRD	X-ray diffraction
PL	Photoluminescence
UV, VIS	Ultraviolet, Visible
IR	Infrared
FWHM	Full width at half maxima
CW	Continuous Wave
fs	Femtosecond
ps	Picosecond
ns	Nanosecond
GSB	Ground-state bleaching
ESA	Excited-state absorption
PIA	Photo-induced absorption
SE	Stimulated Emission
Nps, NPs	Nanoparticles
QDs	Quantum Dots
NLO	Nonlinear Optics/optical
1PA	One-photon absorption
2PA	Two-photon absorption
3PA	Three-photon absorption
MPA	Multi-photon absorption
TAS	Transient Absorption Spectroscopy
OPA	Optical Parametric Amplifier
TEM	Transmission Electron microscopy
FTIR	Fourier-transform infrared spectroscopy
DLS	Dynamic Light Scattering
AuNps	Gold (Au) nanoparticles
C-AuNps	Chemically synthesized Gold (Au) nanoparticles
L-AuNps	Laser ablated Gold (Au) nanoparticles
GeNps	Germanium (Ge) Nanoparticles
NLA	Nonlinear absorption
NLR	Nonlinear refraction
OA	Open aperture
CA	Closed aperture
RSA	Reverse Saturation of Absorption
SA	Saturation of Absorption