Giant Enhancement of Nonlinear Optical Response in Nd:YAG Single Crystals by Embedded Silver Nanoparticles

Rang Li,† Ningning Dong,‡ Chen Cheng,† Feng Ren,§ René Hübner,∥ Jun Wang,‡ Shengqiang Zhou,∥ and Feng Chen*†§∥

†School of Physics, State Key Laboratory of Crystal Materials, Shandong University, 27 Shanda Nanlu, Licheng District, 250100 Jinan, China
‡Key Laboratory of Materials for High-Power Laser, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, 390 Qinghe Road, Jiading District, 201800 Shanghai, China
§Department of Physics, Center for Ion beam Application and Center for Electron Microscopy, Wuhan University, Bayi Road, Wuchang District, 430072 Wuhan, China
∥Institute of Ion Beam Physics and Materials Research, Helmholtz-Zentrum Dresden-Rossendorf, Bautzner Landstr. 400, 01328 Dresden, Germany

ABSTRACT: We report on the enhancement and modulation of nonlinear optical response in an Nd:Y3Al5O12 (Nd:YAG) laser crystal through embedded silver nanoparticles (NPs) fabricated by Ag⁺ ion implantation. The linear absorption spectrum of the sample clearly reveals a localized surface plasmon resonance (SPR) band from 350 to 700 nm correlated to the Ag NPs. By using the Z-scan technique with femtosecond pulses at a wavelength of 515 nm, which is considered as an optical excitation within the SPR band, the nonlinear refraction index reaches values as high as \(10^{-12}\) cm²/W, enhanced by \(4\) orders of magnitude in comparison to that of unimplanted Nd:YAG (without Ag NPs). In addition, it has been shown that embedded Ag NPs in the Nd:YAG host reveal saturable absorption signifying the nonlinear responses. We have also observed that the nonlinear absorption coefficients depend significantly on the excitation energy and can be modulated by varying the fluence of Ag⁺ ions.

1. INTRODUCTION

Noble metallic nanostructures embedded in a transparent dielectric matrix are of growing interest due to their large third-order optical nonlinearities ascribed to the surface plasmon resonance (SPR) and the quantum size effect.1,2 With the purpose of avoiding reunion and formation of the thermodynamic of bulk materials,3 noble metallic NPs can be embedded in transparent materials by a few developed technologies, such as ion implantation4−7 and sol−gel methods.8 The ion beam technology offers versatile solutions for materials modification and also has been applied for the generation and synthesis of various nanoscale structures.9 For example, by using swift heavy ions, nanotracks can be formed inside the matrix due to the electronic energy deposition of the incident ions onto the target materials.10−12 Since the pioneering work by Davenas et al. in 1973,13,14 in which the synthesis of sodium and calcium NPs in ionic crystals of LiF and MgO was realized, ion implantation has opened a promising avenue to fabricate nanomaterials with desired properties on account of its unique advantages, for instance, the flexibility of the types of metals and substrates and the possibility of fabrication over a large area in a single step and long-time sustainment without deterioration.15,16

In the recent decades, numerous studies have shown that the significant enhancement of optical nonlinearities17−20 as a consequence of collective oscillation of electron gas in metal that couples with electromagnetic fields, makes noble metallic nanocomposites promising as optical data recording disks, optical waveguides,21 and all-optical switches.22 Different from other noble metallic NPs, silver NPs own lower intrinsic loss of plasmonic energy at visible frequencies that gives rise to SPR. Moreover, the SPR energy of silver NPs is far from the interband transition energy so that analyzing the origin of the optical nonlinearities becomes easier.23−25 In-depth researches indicate that the shape of the metallic NPs and their dielectric environment determine the surface frequency and the nonlinear optical (NLO) properties consequently.26−31 Thus, the size, the volume fraction of metal NPs, and the substrate play an essential role in SPR processing.

As one of the major gain media for solid-state laser systems, Nd:YAG possesses superior fluorescence properties, a high...
damage threshold, and a relatively high emission cross-section. In addition to the main applications of bulk lasers, a number of works have been realized based on rare-earth ion-doped YAG, for example, for optical waveguides, signal amplification, and so on. The NPs in this gain medium may offer the possibility of a combination of NLO responses and lasing. In this work, we report on the fabrication of silver nanoparticles (NPs) embedded in Nd:YAG crystals by using ion implantation. We observe an efficient modulation of the NLO response. The morphology of the NPs has been investigated by transmission electron microscopy. In accordance with the result calculated by using the Mie theory, an absorption spectrum has been obtained as well, which indicates the controllable SPR effect obviously. Furthermore, the third-order optical nonlinearities of these samples, including nonlinear absorption and nonlinear refraction, were investigated through the Z-scan setup with femtosecond (fs) pulses at 515 nm, which is located in the SPR band (Figure 1).

2. RESULTS AND DISCUSSION

The simulation of the ion-implantation process with a hundred thousand numbers of Ag+ ions is displayed in Figure 2, which is calculated by the software of SRIM. The 2D depth plot is...
shown in red, and the lateral plot is depicted in green. As we can see, the density of incident ions in the bulk presents a Gauss-like distribution characteristic with a half-width of $\sim 50$ nm. It is worth noting that the distribution center of Ag$^+$ ions is 57 nm, with a total range of around 100 nm.

During the ion-implantation process, the implanted ion will be randomly embedded in the crystal when the concentration is below the solubility limit. However, when the implantation dose is high and the implanted impurity atoms are not miscible with the substrate, these implanted atoms can aggregate to form nanoclusters. The formation of NPs can occur already during implantation if the implanted dose is higher than a certain threshold and if their diffusion in the substrate is fast. If the diffusion coefficient of the impurity atoms is low during implantation, a post-implantation annealing initiates the precipitation of nanoclusters. In both cases, the NPs can grow and coarsen to bigger particles with increasing impurity concentration and annealing temperature/time. This has been well documented for many metal ions implanted in oxides, such as Au in SiO$_2$.

Figure 3a depicts the absorption spectrum of the Ag NPs embedded in Nd:YAG crystals. For the sample with the highest fluence, the phenomenon of the resonance interaction is obvious, whereas the absorption peak is quite gentle for samples 3 and 4 with lower fluences. Therefore, the NLO property study will focus on the two higher-fluence Ag$^+$-implanted samples. As shown in Figure 3, the absorption peaks are at 497 and 505 nm for samples 2 and 1, respectively, and sample 1 performs a stronger absorption compared to that of the other samples. It is reasonable on the basis of previous relevant literature. The higher dose of implanted ions results in a larger NP size, leading to the red shift of the absorption peak. Figure 3b is the calculation of the peak positions of different sizes of Ag NPs by the Mie theory using the formula...

![Figure 3](image-url)
γ = \frac{18 \pi p_0 e_m^{3/2}}{\lambda_0} \frac{\varepsilon_m''}{|\varepsilon_m'' + 2\varepsilon_d|^2} \tag{1}

where \( \varepsilon_m, \varepsilon_d, \) and \( p \) are the complex dielectric constants of the metal and the insulator and the volume fraction of the metal, respectively. \( \varepsilon_m'' \) and \( \lambda_0 \) denote the imaginary part of \( \varepsilon_m \) and the wavelength of light in vacuum, respectively. In the case of SPR, \( \varepsilon_m''(\omega) + 2\varepsilon_d'(\omega) = 0 \), which is just the condition for maximum absorption. As shown in Figure 3b, the peak position has a red shift as the diameter of the NPs increases. It coincides with our result, although the shift is a little smaller than that in the experimental data. The reason we believe this is that the Ag NPs are not regular during the ion-implantation processing and the shape may not be an absolute sphere, which is essential to the absorption.

Figure 4a shows a cross-sectional overview bright-field transmission electron microscopy (BF-TEM) micrograph of sample 2. Besides amorphization of an approximately 160 nm thick surface layer, Ag+ ion implantation of an Nd:YAG crystal at a fluence of \( 5 \times 10^{16} \) ions/cm\(^2\) leads to the formation of an approximately 75 nm wide NP-containing band centered at around 60 nm below the sample surface. The NPs are of almost a spherical shape with a slightly varying size distribution, as shown in the lower inset of Figure 4a. Furthermore, the high-resolution TEM (HRTEM) micrograph points to the formation of crystalline NPs. Calculating the corresponding diffractogram by Fast Fourier Transformation gives two rings of Bragg reflections, which can be assigned to polycrystalline silver (upper inset of Figure 4a). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging coupled with qualitative chemical analysis by energy-dispersive X-ray spectroscopy (EDXS), as shown in Figure 4b, confirms the observations regarding the formation of Ag NPs.

Figures 5a,b shows the excitation pulse energy-dependent OA Z-scan results of Ag+ ion-implanted Nd:YAG crystals with the dose of \( 1 \times 10^{17} \) and \( 5 \times 10^{16} \) ions/cm\(^2\), respectively. As we can see, the normalized transmittance curves exhibit symmetrical peaks on the laser focal point (i.e., \( z = 0 \)), indicating clear saturable absorption (SA) responses in these two samples, and the SA behavior becomes much more pronounced as the pulse energy increases. Figure 5c gives the SA response of sample 1, sample 2, and the pure Nd:YAG crystal at an irradiance pulse energy of 150 nJ, which exhibits the dependence on fluence of the implanted ions. The higher-fluence Ag+-doped sample has a larger SA response of \( \sim 70\% \) comparing to \( \sim 14\% \) for the lower one. And it should be pointed out that we did not observe any prominent NLO response from the pure Nd:YAG crystal. As a consequence, the SA performances mainly originate from the Ag NPs, which can attribute to SPR, and we can modulate the SA performances through the fluence of the implanted ions. On the basis of the NLO theory, the propagation equation in these samples can be written as: \( dl/dz' = -\alpha_d - \alpha_{NL} I \), where \( I \) is the excitation intensity, \( z' \) is the propagation distance in the samples, \( \alpha_d \) is the linear absorption coefficient, and \( \alpha_{NL} \) is the nonlinear absorption coefficient. This equation can be solved as follows\(^{42}\).
where $q_0(z) = \alpha_{NL}(L_{\text{eff}})/(1 + z^2/z_0^2)$, $L_{\text{eff}} = [1 - e^{-\sigma_0 L_0}] / \alpha_0$, $L_0$ is the effective thickness of the Ag NPs layer, $L$ is the layer thickness of the Ag NPs, $I_0$ is the light intensity at the focus, and $z_0$ is the beam’s diffraction length. By fitting the open-aperture (OA) Z-scan results, we can obtain the $\alpha_{NL}$ of these samples, and the negative value represents the SA response (Figure 5d). It is clear that the absolute value of $\alpha_{NL}$ decreases steadily as the excitation pulse energy increases in both the $5 \times 10^{16}$ and $1 \times 10^{17}$ ions/cm$^2$ Ag$^+$ ion-implanted Nd:YAG crystals. Furthermore, we can see the sample with $1 \times 10^{17}$ ions/cm$^2$ Ag$^+$-implantation possesses larger $\alpha_{NL}$ than the $5 \times 10^{16}$ ions/cm$^2$ one; for example, the coefficient is $\sim 2000$ cm/GW for sample 1 at 150 nJ, whereas it is $\sim 360$ cm/GW for sample 2, which illustrates the superior SA performance in the higher-fluence Ag$^+$ ion-implanted sample. This is consistent with the result in Figure 5c.}

Considering the possibility that the nonlinear effects may be caused by higher-order nonlinearities rather than third-order nonlinearities, we plot the linear fit of the curve of $\ln(T(z) - 1)$ versus $\ln(I_0)$ (i.e., $\ln(T(z) - 1)$ as a function of $\ln(I_0)$), where $I_0$ is the excitation intensity at position $z$. If the slope of the fitting line is 1, the nonlinear phenomena are due to the third-order nonlinearities. As one can see, the slopes in Figure 6a are all equal to $\sim 1.0$ at low energies (less than 100 nJ), whereas it reaches 1.1 at 150 nJ for the sample with Ag$^+$ implantation at a fluence of $5 \times 10^{16}$ ions/cm$^2$. For the sample with the fluence of $1 \times 10^{17}$ Ag$^+$ ions/cm$^2$ (Figure 6b), only at an energy of 10 nJ does the slope equal to 1, whereas at medium (50 and 100 nJ) and high energy (150 nJ), the value reaches 1.1 and 1.2, respectively. This suggests that the higher-order nonlinearities are not ignorable for high-energy excitation (150 nJ). In addition, comparing the results of Figure 6a,b, with a higher fluence of the implanted Ag$^+$ ions, it becomes easier to excite the higher-order nonlinearities because of the higher concentration of plasmonic NPs. In addition, we measure the sample with a fluence of $1 \times 10^{17}$ Ag$^+$ ions/cm$^2$ at irradiances 6 and 8 nJ to give a supplement in the low-energy regime (see Figure 6c). The inset of this figure is the linear fit to the plot of $\ln(T(z) - 1)$ versus $\ln(I_0)$. The origin to change in transmittance of about 10% guarantees that the results are corresponding to the third-order optical nonlinearities. As we can see, it shows similar laws compared to the results with higher irradiances. In this way, we can conclude that the nonlinear effects are mainly caused by the third-order nonlinearities within the range of the excitation energy used in this work.

In the meantime, we also investigate the nonlinear refraction properties of these samples. As we all know, the nonlinear index of refraction is contributed to several physical mechanisms, such as electronic polarization, Raman-induced Kerr effect, molecular orientational effects, electrostriction, population redistribution, and thermal contributions. The distortion of...
the electron cloud about an atom or molecule by the optical field, which is involved in the electronic polarization mechanism, is proven to be the main source of the NLO refraction of noble metal nanomaterials.\(^4\) Note that, during the ion-implantation process, ions interact with the surface lattice atoms of the bulk mainly through elastic collisions, which makes the atoms leave the initial lattice position and form the Frenkel defects.\(^5\) In addition, higher doses lead to more serious lattice damage, which may have a strong impact on the self-focusing and/or self-defocusing effects, and this may be the main reason that we did not observe a clear closed-aperture (CA) Z-scan signal in sample 1. It is known that annealing can reduce color centers and lattice damage effectively,\(^6\) hence, the annealing effect will be the next step in our research plan.

Figure 7 shows the CA results of sample 2 and the pure Nd:YAG crystal under different pulse energies, which show a valley-peak type, indicating a self-focusing effect. The nonlinear refractive index, \(n_2\), of these samples can be obtained by fitting the CA Z-scan data by the analytic formula\(^7\)

\[
T_{\text{Norm}}(z) = 1/[(1 - 4x\Delta n_0/((1 + x^2)^{3/2})) + [4\Delta n_0^2/((1 + x^2)^{3/2})]]
\]

where \(\Delta n_0 = k\Delta n \cdot L_{\text{eff}} \cdot z_0 = k\Delta n_0^2/2, \) and \(x = z/z_0\). The deduced \(n_2\) values are summarized in Table 1, with an error bar of approximately ±10%. From Table 1, we can see that sample 2 possesses a giant \(n_2\) reaching ~2 \times 10^{-12} \text{ cm}^2/\text{W}, which is about 4 orders of magnitude larger in comparison to that of pure Nd:YAG with a value of ~1.4 \times 10^{-16} \text{ cm}^2/\text{W}. This is relevant with the fact that the former has Ag NPs, whereas the latter does not. The SPR effect, therefore, enhances the NLO response significantly as reported in some previous works.\(^8\)\(^-\)\(^10\)

It should be noted that, different from these previous works, the nonlinear refractive index of the matrix we used is 10-fold higher than that of the ion-implanted Ag nanoparticles embedded in silica glass.\(^3\)\(^1\) This proves that the nonlinear refractive index of the ion-implanted layer is influenced not only by the implanted ions but also by the matrix.

### 3. CONCLUSIONS

Using ion implantation, we have fabricated Ag NPs embedded in an Nd:YAG crystal, as confirmed by TEM analysis. The linear and NLO responses have been investigated. The absorption spectrum shows the stronger absorbance of higher-fluence Ag\(^+\) ions with the peak at around 500 nm, which basically coincides with calculation by the Mie theory. The NLO properties have been studied by a Z-scan system with both open and closed apertures. The nonlinear absorption coefficient of the sample with 5 \times 10^{10} ions/cm\(^2\) fluence is estimated to be ~368.2 cm/GW at 150 nJ, and it increases with the decrease in pulse energy. Moreover, the nonlinear refraction is enhanced by 4 orders of magnitude with respect to pure Nd:YAG. With the higher-dose implantation (1 \times 10^{17} ions/cm\(^2\)), the nonlinear absorption coefficient has over 5 times more than that of the sample with low-fluence implantation.

### 4. EXPERIMENTAL SECTION

Nd:YAG crystals (purchased from ATOM OPTICS Company) doped with 1 at% Nd\(^3\) ions were implanted with 200 keV Ag\(^+\) ions at four different fluences of 1 \times 10^{16}, 5 \times 10^{16}, 3 \times 10^{16}, and 1 \times 10^{16} ions/cm\(^2\) (samples 1–4) by analytical-type ion-implanter LC22-1C0-01. This process generated a surface layer of embedded Ag NPs in the bulk, which is 100 nm in thickness according to the calculation by SRIM.\(^2\) As seen in Figure 1a, the Ag\(^+\) ion beam was tilted by 7\(^\circ\) off the vertical plane of the sample surface to minimize the channeling effect.\(^3\)

To locally analyze the microstructure of the Nd:YAG crystal implanted with Ag\(^+\) ions at a fluence of 5 \times 10^{16} ions/cm\(^2\), TEM investigations were carried out using an image C\(_e\)-corrected Titan 80-300 microscope (FEI) operated at an accelerating voltage of 300 kV. Besides BF-TEM and HRTEM, atomic number contrast imaging by HAADF-STEM was performed. For qualitative chemical analysis, EDXS was performed with a Li-doped silicon detector (EDAX) attached to the Titan microscope. Before TEM analysis, the specimen mounted in a double-tilt analytical holder was placed for 10 s into a Model 1020 Plasma Cleaner (Fischione) to remove organic contamination. A classical cross-sectional TEM specimen was prepared by sawing, grinding, dimpling, and final Ar ion milling.

Absorption spectra were measured using a U4100 UV−vis−NIR spectrophotometer and were compared with calculations based on the Mie theory. A typical OA and CA Z-scan system, with the schematic shown in Figure 1b, was used to study the third-order nonlinear optical (NLO) properties of these Ag\(^+\) ion-embedded Nd:YAG crystals. In this technique, the transmittance through the sample as a function of the incident laser intensity was measured as the sample gradually moved through the focus of a lens along the laser propagation direction (\(z\) axis). All measurements were carried out by using 340 fs pulses from a fiber laser operating at 515 nm, with a repetition rate of 100 Hz. The laser beam was tightly focused through a 15 cm focal-length lens, and the beam waist radius was estimated to be ~15 \(\mu\)m at the focus. For comparison, different input pulse energies were chosen, within the range of 6 to 150 nJ.

### AUTHOR INFORMATION

**Corresponding Author**

*E-mail:* drfchen@sdu.edu.cn.

**ORCID**

Feng Ren: 0000-0002-9557-5995

Feng Chen: 0000-0002-9277-9810

**Notes**

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

This work is financially supported by the National Natural Science Foundation of China (No. 11535008), the Strategic Priority Research Program of CAS (XDB16030700), and the Key Research Program of Frontier Science of CAS (QYZDB-SSW-JSC041). The support by the Structural Characterization Facilities Rossendorf at IBC is gratefully acknowledged.

### REFERENCES

1. Hou, W.; Cronin, S. B. A Review of Surface Plasmon Resonance-Enhanced Photocatalysis. *Adv. Funct. Mater.* 2013, 23, 1612−1619.
(2) Jiang, F.; Chen, D.; Li, R.; Wang, Y.; Zhang, G.; Li, S.; Zheng, J.; Huang, N.; Gu, Y.; Wang, C.; Shu, C. Eco-Friendly Synthesis of Size-Controlable Amine-Functionalized Graphene Quantum Dots with Antimycoplasmoha Properties. *Nanoscale* 2013, *S*, 1137−1142.

(3) Xiang, W.; Gao, H.; Ma, L.; Ma, X.; Huang, Y.; Pei, L.; Liang, X. Valence State Control and Third-Order Nonlinear Optical Properties of Copper Embedded in Sodium Borosilicate Glass. *ACS Appl. Mater. Interfaces* 2015, *7*, 10162−10168.

(4) Carles, R.; Farcau, C.; Bonafos, C.; Benassayag, G.; Bayle, M.; Benzo, P.; Groenen, J.; Zwick, A. Three Dimensional Design of Silver Nanoparticle Assemblies Embedded in Dielectrics for Raman Spectroscopy Enhancement and Dark-Field Imaging. *ACS Nano* 2011, *8*, 8774−8782.

(5) Chen, H.; Wang, Y.; Zhang, X.; Song, S.; Chen, H.; Zhang, K.; Xiong, Z.; Ji, L.; Dai, H.; Wang, D.; Lu, J.; Wang, R.; Zheng, L. Structure analysis of bimetallic Co-Au nanoparticles formed by sequential ion implantation. *Appl. Surf. Sci*. 2016, 378, 191−195.

(6) Wood, K. N.; Pylypenko, S.; Olson, T. S.; Dameron, A. A.; O’Neill, K.; Christensen, S. T.; Dinh, H. N.; Gennett, T.; O’Hayre, R. Effect of Halide-Modified Model Carbon Supports on Catalyst Stability. *ACS Appl. Mater. Interfaces* 2012, *4*, 6728−6733.

(7) Can-Uc, B.; Rangel-Rojo, R.; Pena-Ramirez, A.; de Araujo, C. B.; Baltar, H. T. M. C. M.; Crespo-Sosa, A.; Garcia-Betancourt, M. L.; Oliver, A. Nonlinear optical response of platinum nanoparticles and platinum ions embedded in sapphire. *Opt. Express* 2016, *24*, 9955−9965.

(8) Mitra, S.; Mandal, K.; Kumar, P. Temperature dependence of magnetic properties of NiFe2O4 nanoparticles embedded in SiO2 matrix. *J. Magn. Magn. Mater.* 2006, *306*, 254−259.

(9) Werner, W.; Wendler, E., Eds.; *Ion Beam Modification of Solids*; Springer, 2016.

(10) Gruber, E.; Salou, P.; Bergen, L.; Kharrazi, M. E.; Lattouf, E.; Gygryel, C.; Wang, Y.; Benyagoub, A.; Levassas, D.; Rangama, J.; Lebus, H.; Ban-d’Etat, B.; Schleberger, M.; Aumayr, F. Swift heavy ion irradiation of CaF2— from grooves to hillocks in a single ion track. *J. Phys.: Condens. Matter* 2016, *28*, No. 405001.

(11) Turel, M.; Thevenard, P.; Gassagne, G.; Hobbs, L. H. Observation of implanted potassium aggregates in MgO single crystals. *Phys. Status Solidi A* 1978, *48*, 425−430.

(12) Rodriguez, M. D.; Li, W. X.; Chen, F.; Trautmann, C.; Bierschenk, T.; Afra, B.; Schardey, D.; Ewing, R. C.; Mudie, S. T.; Kharrazi, M. E.; Lattouf, E.; Werner, W., Wendler, E., *eds.*; *Ion Beam Modification of Solids*; Springer, 2016.

(13) Davenas, J.; Perez, A.; Thevenard, P.; Dupuy, C. H. S. Correlation between absorption bands and implanted alkali ions in LiF. *Phys. Status Solidi A* 1973, *19*, 679−686.

(14) Silva-Pereyra, H. G.; Arenas-Alatorre, J.; Rodriguez-Fernandez, L.; Crespo-Sosa, A.; Cheang-Wong, J. C.; Reyes-Esqueda, J. A. Oliver High stability of the crystalline configuration of Au nanoparticles embedded in silica under ion and electron irradiation. *J. Nanopart. Res.* 2010, *12*, 1787−1795.

(15) Stepanov, A. L. Nonlinear optical properties of implanted metal nanoparticles in various transparent matrices: A Review. *Rev. Adv. Mater. Sci.* 2011, *27*, 115−145.

(16) Toroghi, S.; Lumdee, C.; Kik, P. G. Heterogeneous plasmonic trimmers for enhanced nonlinear optical absorption. *Appl. Phys. Lett.* 2015, *106*, No. 103102.

(17) Shorokhov, A. S.; Melik-Gaykazyan, E. V.; Smirnova, D. A.; Hopkins, B.; Chong, K. E.; Choi, D. Y.; Schcherbakov, M. R.; Miroshnichenko, A. E.; Neshev, D. N.; Fedyanin, A. A. Multifold Enhancement of Third-Harmonic Generation in Dielectric Nanoparticles Driven by Magnetic Fano Resonances. *Nano Lett.* 2016, *16*, 4857−4861.

(18) Yu, X. X.; Wang, Y. H. Measurement of nonlinear optical refraction of composite material based on sapphire with silver by Kerr-lens autocorrelation method. *Opt. Express* 2014, *22*, 177−182.

(19) Grinblat, G.; Li, Y.; Nielsen, M. P.; Oulton, R. F.; Maier, S. A. Enhanced Third Harmonic Generation in Single Germanium Nanodisks Excited at the Anapole Mode. *Nano Lett.* 2016, *16*, 4635−4640.

(20) Mengin, S.; Gottwald, M.; Lambert, C. H. L.; Steil, D.; Uhliř, V.; Pang, L.; Henn, M.; Alebrand, S.; Cinchetti, M.; Malinowski, G.; Fainman, Y.; Aeschlimann, M.; Fullerton, E. E. Engineered Materials for All-Optical Helicity-Dependent Magnetic Switching. *Nat. Mater.* 2014, *13*, 286−292.

(21) Zeng, H.; Qiu, J.; Ye, Z.; Zhu, C.; Gan, F. Irradiation Assisted Fabrication of Gold Nanoparticles-Doped Glass. *J. Cryst. Growth* 2004, *267*, 156−160.

(22) Reyna, A. S.; de Araujo, C. B. An optimization procedure for the design of all-optical switches based on metal-dielectric nano- composites. *Opt. Express* 2015, *23*, 7659−7666.

(23) Boltasseva, A.; Atwater, H. A. Low-loss planar metamaterials. *Science* 2011, *331*, 290−291.

(24) Ganev, R. A.; Rysanyansky, A. I.; Stepanov, A. L.; Usmanov, T. Saturated absorption and nonlinear refraction of silicate glasses doped with silver nanoparticles at S2 nm. *Opt. Quantum Electron.* 2004, *36*, 949−960.

(25) Segonds, P.; Boulanger, B.; Menaert, B.; Zaccaro, J.; Salvestrini, J. P.; Fontana, M. D.; Moncorge, R.; Poree, F.; Gadret, G.; Mengin, J.; Breiner, A.; Boulon, G.; Aka, G.; Pelenc, D. Optical characterizations of YCa4(BO3)3 and Nd:YCa4(BO3)3 crystals. *Opt. Mater.* 2007, *29*, 975−982.

(26) Sato, S.; Ohnma, M.; Oyoshi, K.; Takeda, Y. Experimental investigation of nonlinear optical properties of Ag nanoparticles: Effects of size quantization. *Phys. Rev. B* 2014, *90*, No. 125417.

(27) Lu, J.; Prabhu, M.; Song, J.; Li, C.; Xu, J.; Ueda, K.; Kaminskii, A. A.; Yagi, H.; Yanagitani, T. Optical properties and highly efficient laser oscillation of Nd:YAG ceramics. *Appl. Phys. B: Lasers Opt.* 2000, *71*, 469−473.

(28) Okhrimchuk, A. G.; Obraztsov, P. A. 11-GHz waveguide Nd:YAG laser CW mode-locked with single-layer graphene. *Sci. Rep.* 2015, *5*, No. 11172.

(29) Zeng, Z. P.; Garoufalis, C. S.; Teras, A. F.; Baskoutas, S. Line and nonlinear optical properties of ZnO/ZnS and ZnS/ZnO core shell quantum dots: Effects of shell thickness, impurity, and dielectric environment. *J. Appl. Phys.* 2013, *114*, No. 023510.

(30) Salamu, G.; Jipa, F.; Zamfirescu, M.; Pavel, N. Watt-Level Output Power Operation From Diode-Laser Pumped Circular Buried Depressed-Cladding Waveguides Inscribed in Nd:YAG by Direct Femtosecond-Laser Writing. *IEEE Photonics J.* 2016, *8*, No. 1500209.

(31) Simoens, S.; Niquet, N.; Peeters, G.; Swinnen, G.; Verheir, H.; Govaerts, Y.; Verhulst, Y.; Verbist, K.; Robert, E.; Houbiers, R.; Govaerts, Y.; Verbist, K. Femtosecond-Laser Writing. *Science* 2017, *2*, 1286.

(32) Lu, J.; Prabhu, M.; Song, J.; Li, C.; Xu, J.; Ueda, K.; Kaminskii, A. A.; Yagi, H.; Yanagitani, T. Optical properties and highly efficient laser oscillation of Nd:YAG ceramics. *Appl. Phys. B: Lasers Opt.* 2000, *71*, 469−473.
(38) Gonella, F. Nanoparticle formation in silicate glasses by ion-beam-based methods. *Nucl. Instrum. Methods Phys. Res., Sect. B* 2000, 166−167, 831−839.

(39) Stepanov, A. L.; Khaibullin, I. B. Fabrication of metal nanoparticles in sapphire by low-energy ion implantation. *Rev. Adv. Mater. Sci.* 2005, 9, 109−129.

(40) Ren, F.; Jiang, C. Z.; Wang, J. B.; Liu, C.; Oku, T. Controlling the morphology of Ag nanoclusters by ion implantation to different doses and subsequent annealing. *Phys. Rev. Lett.* 2006, 97, No. 165501.

(41) Stepanov, A. L.; Popok, V. N.; Khaibullin, I. B.; Kreibig, U. *Nucl. Instrum. Methods Phys. Res., Sect. B* 2002, 191, 473−477.

(42) Sheik-Bahae, M.; Said, A. A.; Wei, T. H.; Hagan, D. J.; Van Stryland, E. W. Sensitive measurement of optical nonlinearities using a single beam. *IEEE J. Quantum Electron.* 1990, 26, 760−769.

(43) He, J.; Qiu, Y. L.; Li, H. P.; Mi, J.; Ji, W. Three-photon absorption in ZnO and ZnS crystals. *Opt. Express* 2005, 13, 9235−9247.

(44) Sutherland, R. L. Nonlinear Index of Refraction. In *Handbook of Nonlinear Optics*, 2nd ed.; Thompson, B. J., Ed.; Marcel Dekker: New York, 2003; pp 343−368.

(45) Pelaz, L.; Marques, L. A.; Barbolla, J. Ion-beam-induced amorphization and recrystallization in silicon. *J. Appl. Phys.* 2004, 96, 5947.

(46) Benayas, A.; Dong, N. N.; Yao, Y. C.; Chen, F.; Bettiol, A. A.; Jaque, D. Thermal optimization and erasing of Nd:YAG proton beam written waveguides. *Opt. Lett.* 2011, 36, 3278−3280.

(47) Kwak, C. H.; Lee, Y. L.; Kim, S. G. Analysis of asymmetric Z-scan measurement for large optical nonlinearities in an amorphous As$_2$S$_3$ thin film. *J. Opt. Soc. Am. B* 1999, 16, 600−604.

(48) Henari, F. Z.; Dakhel, A. A. Linear and nonlinear optical properties of gold nanoparticle-Eu oxide composite thin films. *J. Appl. Phys.* 2008, 104, No. 033110.

(49) Kohlgraf-Owens, D. C.; Kik, P. G. Numerical study of surface plasmon enhanced nonlinear absorption and refraction. *Opt. Express* 2008, 16, 10823−10834.

(50) Wang, Y. H.; Yu, X. X.; Liu, F.; Wang, Y. M. Nonlinear refraction of lithium niobate crystal doped with different metal nanoparticles. *Mater. Lett.* 2014, 123, 35−37.

(51) Torres-Torres, C.; Perea-Lopez, N.; Reyes-Esqueda, J. A.; Rodriguez-Fernandez, L.; Crespo-Sosa, A.; Cheang-Wong, J. C.; Oliver, A. Ablation and optical third-order nonlinearities in Ag nanoparticles. *Int. J. Nanomed.* 2010, 5, 925−932.

(52) Ziegler, J. F. Computer Code, SRIM. http://www.srim.org.

(53) Jia, Y.; Tan, Y.; Cheng, C.; de Aldana, J. R. V.; Chen, F. Efficient lasing in continuous wave and graphene Q-switched regimes from Nd:YAG ridge waveguides produced by combination of swift heavy ion irradiation and femtosecond laser ablation. *Opt. Express* 2014, 22, 12900−12908.