

PACS numbers: 42.65.Ky; 83.70.Hq
DOI: 10.1070/QE2001v031n02ABEH001914

Third-harmonic generation of a picosecond Nd:YAG laser in colloidal solutions of platinum and copper

R A Ganeev, A I Ryasnyanskii, T Usmanov

***Abstract*. Third-harmonic generation of laser radiation is studied in colloidal solutions of platinum and copper. The values of $\chi^{(3)}$ in these solutions at a wavelength of 1064 nm were measured to be 2×10^{-14} and 10^{-14} CGSE units, and the efficiency of the Nd : YAG laser radiation conversion to the third harmonic was 7×10^{-7} and 3×10^{-7}, respectively.**

***Keywords*:** *third-harmonic generation, colloidal solutions, picosecond radiation.*

The interest in colloidal solutions stems from the possibility of their practical and scientific applications (optical limiting, optoelectronics, etc.). The use of such media in optoelectronics is made feasible by their strong and fast nonlinear optical response to the external action. The aggregation of colloidal metal microparticles increases the nonlinear optical response and, in particular, results in a significant increase in the intensity of degenerate four-photon scattering [1]. The latter is due to the growth of the amplitude of local fields in fractal clusters with a high polarisability. The nonlinear optical characteristics of colloidal solutions of metals were studied in several papers (see, e.g., Refs [2–4]). Note, however, that papers devoted to the conversion of laser radiation frequency in such media are absent.

We present below the results of our investigation of the third-harmonic generation (THG) in colloidal solutions of platinum and copper employing the picosecond radiation of a Nd : YAG laser. The nonlinear susceptibilities and the conversion efficiency of this process were determined for these media.

The duration of a 1064-nm Nd : YAG-laser pulse was 35 ps and the energy was 2 mJ. The radiation was focused by a lens with a focal length of 25 cm into a cell with a colloidal solution 5 mm thick and recorded with a calibrated FD-24K photodiode and a V4-17 digital voltmeter. The converted 354.7-nm radiation was separated with UFS-2 filter from the pump radiation and directed to a DFS-452 diffraction spectrograph equipped with a FEU-106 photomultiplier and a V4-17 digital voltmeter. The instrumentation in use was calibrated employing the THG in a KDP crystal to measure the absolute values of conversion efficiency in colloidal solutions.

The colloidal solutions were prepared in the following way. The initial material for the preparation of a reference colloidal solution was metal platinum, 0.1 g of which were dissolved in several millilitres of a mixture of nitric and hydrochloric acids upon heating. After evaporation of the solution, the dry residual was again dissolved in 20 ml of diluted (1 : 1) hydrochloric acid. As a result, one millilitre of the solution contained one milligram of platinum.

To prepare a reference solution of colloidal copper, four grams of $CuSO_4$ were dissolved in one litre of distilled water. In this case, one millilitre of the solution contained one milligram of copper. According to the electron microscope analysis, the dimensions of metal clusters ranged from 10 to 60 nm, depending on the degree of metal aggregation.

Fig. 1 shows the dependence of the third-harmonic (TH) signal on the pump intensity for colloidal platinum. The slope of the dependence $I_{3\omega}(I_\omega)$ was equal to 2.8 throughout the intensity range studied, which is close to the result expected in theory (3.0). The experiments were conducted for intensities below the optical breakdown threshold for colloidal solutions ($I_b = 4 \times 10^{11}$ W cm^{-2}). The maximum pump–TH radiation conversion efficiencies for colloidal platinum and copper were 7×10^{-7} and 3×10^{-7}, respectively.

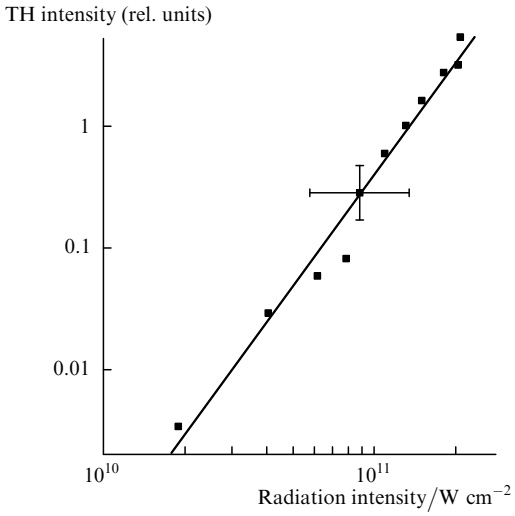

Figure 1. Dependence of the TH signal on the pump radiation intensity for colloidal platinum.

R A Ganeev, T Usmanov 'Akadempribor' Research and Production Association, 700143 Tashkent, Uzbekistan; e-mail: ganeev@acpr.silk.org
A I Ryasnyanskii A Navoi Samarkand State University, 703004 Samarkand, Uzbekistan

Received 11 October 2000
Kvantovaya Elektronika **31** (2) 185–186 (2001)
Translated by E N Ragozin

An attempt to accomplish the pump-to-TH radiation conversion in several other colloidal solutions (colloidal silver and colloidal gold) did not meet with success.

To obtain phase matching in the THG upon the interaction between plane waves, the condition $\Delta k = k_3 - 3k_1 = 0$ should be fulfilled (here, $\boldsymbol{k}_3$ and $\boldsymbol{k}_1$ are the wave vectors of the harmonic and the pump radiation). Our experimental conditions corresponded to this case. The confocal parameter of radiation focused by a lens with a focal length of 25 cm was 23 mm for a nonlinear medium 5 mm in length, i.e., the conversion occured upon the interaction between plane waves.

It is known that the condition $\Delta k = 0$ can be satisfied only when the frequency of the generated harmonic falls within the range of anomalous medium dispersion [5]. In the 354.7-nm range, both colloidal platinum and colloidal copper exhibit the normal dispersion. This conclusion was made from the investigation of absorption spectra of these media. The optical characteristics of metal aggregates are determined by the dependence of the frequency variation rate of plasma oscillations and their long-wavelength wing on the degree of aggregation [6].

This parameter, which was introduced in Ref. [4], is based on several theoretical and experimental studies of the dependence of spectral absorption of colloidal metals in the vicinity of the plasma resonance on the degree of aggregation. The broadening of the absorption spectra of cluster colloids is caused by the interaction of the multipoles induced by the electromagnetic field in metal clusters [7].

Therefore, the process that we observed took place under the conditions far from the phase matching. In this case, the nonlinear susceptibility responsible for the THG is describeded by the expression [8]

$$\left|\chi^{(3)}\right|^2 = \frac{\lambda_1^2 n_3 n_1^3 c^2 \eta}{256\sqrt{3}(\ln^3 2)\pi^5 L^2 I_\omega^2}\left[\frac{\sin(\Delta kL/2)}{\Delta kL/2}\right]^{-2}, \qquad (1)$$

where λ_1 and I_ω are the wavelength and the intensity of the pump radiation, respectively; n_1 and n_3 are the refractive indices at the pump radiation and TH wavelengths, respectively; c is the speed of light; η is the conversion efficiency; L is the length of the nonlinear medium; and $\Delta k = 6\pi(n_3 - n_1)/\lambda_1$ is the difference of the wave vectors of the harmonic and pump radiation.

The nonlinear susceptibilities of the colloidal solutions of Pt and Cu, determined from expression (1) taking into account our experimental conditions, were 2×10^{-14} and 10^{-14} CGSE units, respectively.

We estimated the changes in the phase characteristics of the THG in these media caused by the high-frequency Kerr effect. The nonlinear refractive index n_2 of the colloidal solutions was measured using a conventional technique [9]. Its value at a wavelength of 1064 nm was found to be 1.1×10^{-14} and 4.2×10^{-14} CGSE units for colloidal platinum and colloidal copper, respectively. According to the our calculations, this nonlinear contribution to the refractive index should not have a significant effect on the cubic dependence $I_{3\omega}(I_\omega)$ under the intensities involved.

Note that we observed a similar deviation in fullerene C_{70}-doped polyimide films possessing significantly higher nonlinear contributions to the refractive index. A similar deviation was also observed in the case of strong focusing in gaseous media [10, 11], when the high-frequency Kerr effect was responsible for a phase mismatch and a lowering of the TH intensity growth rate with increasing pump intensity. Note that the reverse situation is also possible, when the phase parameter $\sin^2(\Delta kL/2)/(\Delta kL/2)^2$ increases with the pump intensity owing to the wave detuning in media with the positive n_2. This may result in the optimal phase matching upon THG [11].

References

1. Butenko A V, Shalaev V M, Shtokman M I *Zh. Eksp. Teor. Fiz.* **94** (1) 107 (1988)
2. Danilova Yu E, Drachev V P, Perminov S V, Safonov V P *Izv. Ross. Akad. Nauk Ser. Fiz.* **60** (3) 18 (1996)
3. Karpov S V, Popov A K, Slabko V V *Izv. Ross. Akad. Nauk Ser. Fiz.* **60** (6) 43 (1996)
4. Mehendale S C, Mishra S R, Bindra K S, Langhate M, Dhami T S, Rustagi K C *Opt. Commun.* **133** 273 (1997)
5. Reintjes J F *Nonlinear Optical Parametric Processes in Liquids and Gases* (New York: Academic Press, 1984)
6. Karpov S V, Bas'ko A A, Koshelev S V, Popov A K, Slabko V V *Kolloidn. Zh.* **59** 765 (1997)
7. Markel' V A, Muratov L S, Shtokman M I *Zh. Eksp. Teor. Fiz.* **98** 819 (1990) [*Sov. Phys. JETP* **71** (3) 455 (1990)]
8. Kulagin I A, Usmanov T *Kvantovaya Elektron.* **25** 1121 (1998) [*Quantum Electron.* **28** (12) 1089 (1998)]
9. Sheik-Bahae M, Said A A, Wei T, Hagan D J, van Stryland E W *IEEE J. Quantum Electron.* **26** 760 (1990)
10. Zych L J, Young J F *IEEE J. Quantum Electron.* **14** 147 (1978)
11. Ganeev R A, Kulagin I A, Begishev I A, Redkorechev V I, Usmanov T *Nonlinear Opt.* **16** 109 (1996)