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Passive laser *Q* switches made of glass doped with oxidised nanoparticles of copper selenide

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Abstract. **Passive *Q* switching of Nd^{3+} : YAG ($\lambda =$ 1060 nm) and $YAlO_3 : Nd^{3+}$ (1340 nm) lasers, as well as of an Er^{3+} (1540 nm) glass laser was realised by using glass doped with oxidised nanoparticles of copper selenide. Nonlinear optical properties of the nanoparticles (radius of 25 nm) in a glass matrix were studied by the picosecond absorption spectroscopy technique.**

1. Introduction

At present, various glasses containing nanoparticles of semiconductor compounds are widely used to build passive switches for *Q* switching and mode locking in solid-state lasers. The glass with CdS_xSe_{1-x} nanoparticles has been used as a passive switch in ruby ($\lambda = 694$ nm) and $Cr^{3+} : LiCaAlF_6$ (800 – 900 nm) lasers [1 – 3] and for mode synchronisation in a sapphire – titanium (780 – 870 nm) laser [4, 5]. Mode locking was also reported in Nd (1060 – 1080 nm) lasers and in a forsterite (1200 – 1300 nm) laser through the use of glasses containing nanoparticles of $CuInS_{2x}Se_{2(1-x)}$ and PbS, respectively [6 – 8].

It has been shown [9 – 11] that the materials based on oxidised nanoparticles of CuS, $CuInS_2$, and $CuFeS_2$ are promising media for passive switches within the 800 – 2000 nm spectral range. The oxidation of nanoparticles of these compounds brings about an additional absorption band with a maximum near 1000 nm, which becomes transparent because of the action of laser pulses. In the present work we investigate the saturation of absorption in glasses impregnated with nanoparticles of copper selenide by sol-gel technology. These glasses are used as passive *Q* switches in Nd ($\lambda = 1060$ and 1340 nm) lasers and in an Er^{3+} (1540 nm) glass laser.

The glasses studied in this work were prepared by the sol – gel processing technique described elsewhere [12]. The initial sol was prepared by intermixing tetraethoxylane, ethyl alcohol, water, and hydrochloric acid in the molar ratio 1 : 6 : 10 : 0.08. After adding ammonia to ensure a pH = 7 – 8, the mixture was heated in a closed container up to 1000 °C for about one hour until porous xerogels were formed. The average size of pores was between 100 and 200 nm. As a result of xerogel impregnation with copper nitrate solution and subsequent warming-up, the copper oxide formed inside the xerogels was reduced in the hydrogen atmosphere (600 °C, 1 h) to the metal. Then the xerogels were sealed in glass ampoules together with sufficient elemental selenium to provide a pressure of 1 atm at 1 200 °C.

Following the warming up of the ampoules at 1 200 °C, the xerogels were vitrified to produce a quartz glass stained by oxidised particles of copper selenide. The chemical composition of nanoparticles can be judged from the data obtained earlier for quartz films made by a similar technique. x-Ray diffraction analysis of the films showed the emergence of Cu_2Se [13]. It should also be mentioned that the optical absorption spectra of such films are similar to those of glasses studied here. The mean radius of the nanoparticles measured by electron microscopy was 25 nm with a standard deviation of ~30% from the mean value.

2. Nonlinear-optical properties of glasses doped with oxidised Cu_2Se nanoparticles

Fig. 1 shows the absorption spectra of investigated glass samples containing oxidised nanoparticles (ONPs) and non-oxidised particles of Cu_2Se. According to Ref. [14], the energy gap in Cu_2Se is caused by indirect transitions and is 1.2 eV wide ($\lambda = 1030$ nm). The oxidation of nanoparticles results in the appearance of a broad absorption band *A* with the maximum at $\lambda \sim 1000$ nm whose spectral width

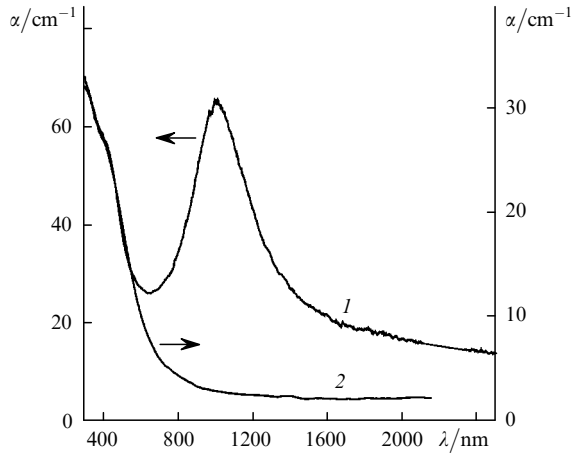

Figure 1. Absorption spectra of glasses prepared by sol – gel processing technology: samples with oxidised (*1*) and non-oxidised (*2*) Cu_2Se nanoparticles.

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at half-maximum is about 450 nm. Similar absorption bands having maxima in the range from 1000 to 1200 nm were observed for ONPs of CuS, $CuInS_2$, $CuFe_2S_3$, $CuFeS_2$ implanted into a polymer film. These bands were ascribed to transitions from low levels emerging within the 'energy gap' as a result of oxidation [9–11]. The origin of such low levels was ascribed to characteristic Cu states appearing on oxidation of nanoparticles [15].

The saturation of absorption in the glass doped with Cu_2Se ONPs was studied at a wavelength of 1060 nm by measuring the transmittance T as a function of the intensity I_0 of pulses falling on the sample. Fig. 2 shows the results obtained with an Nd^{3+}:YAG laser with electro-optical Q switching (20-ns pulses). The optical density measurements by the excitation-sounding technique by using 15-ps pulses with a wavelength of 1080 nm showed that the saturation was restored to its initial value in $\tau \sim 300$ ps, which is considerably less than a laser pulse duration of 20 ns. This fact allowed us to analyse the experimental dependence $T(I_0)$ in terms of the model of a rapidly relaxing absorber [16], which takes into account saturation from the excited state:

$$\alpha(I_0) = \alpha_0\left(1 + \frac{\sigma_2}{\sigma_1}\frac{I_0}{I_s}\right)\left(1 + \frac{I_0}{I_s}\right)^{-1}, \qquad (1)$$

where α is the transmission coefficient; α_0 is the initial transmission coefficient; σ_1 and σ_2 are the absorption cross sections from the ground and excited states, respectively; and $I_s = h\nu/\sigma_1\tau$ is the saturation intensity. The best agreement of the experimental data with the calculated curve was observed for $I_s = 2$ MW cm^{-2} and $\sigma_2/\sigma_1 = 0.36$. From the values of I_s and τ obtained, one can estimate the absorption cross section from the ground state at a wavelength of 1060 nm to be $\sigma_1 \sim 1.6 \times 10^{-16}$ cm^2. As to the absorption from the excited state, it is most probably associated with the electrons captured by traps located at the surface of nanoparticles. A similar induced absorption was observed in the glass doped with Cu_2S nanoparticles [17, 18]. Its relaxation time was ~230 ps, which is close to the value $\tau \sim 300$ ps obtained in the present investigation.

3. Passive Q switching

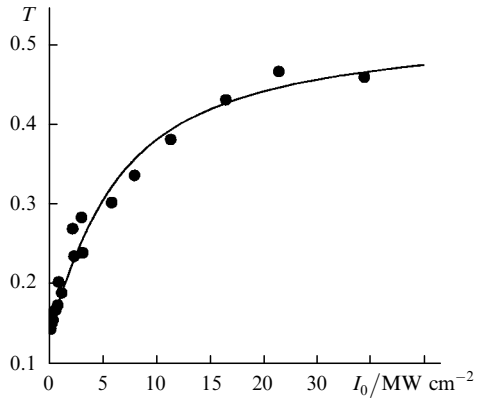

Figure 2. Experimental (dots) and calculated (solid line) transmissions T of glasses doped with Cu_2Se nanoparticles vs the intensity I_0 of impinging pulses with duration 20 ns and $\lambda = 1060$ nm. The sample thickness is 0.3 mm.

The Q switching regime was obtained in Nd^{3+}:YAG ($\lambda = 1060$ nm) and Nd^{3+}:$YAlO_3$ (1340 nm) lasers, as well as in an erbium glass laser (1540 nm) by using a passive switch made of glass doped with Cu_2Se ONPs. The surfaces of passive switches did not have appropriate antireflection coating.

The cavity of the Nd^{3+}:YAG laser (Fig. 3a) formed by a highly reflecting (nontransmitting) mirror with the curvature radius $r = 1$ m and a flat output mirror with the reflection coefficient $R = 60\%$ had the length $\sim 0.95r$. The active element (AE) having the size $\varnothing 5 \times 50$ mm was located near the nontransmitting mirror. The passive switch (PS) had an initial transmission of about 50% and was located between AE and the output mirror. The Q switching regime was realised for the intracavity focusing parameter $A_g/A_a = 1.4$ (where A_g and A_a are the cross section areas of the cavity mode at the AE and PS positions respectively). The pulses observed were 100 ns long (Fig. 3a), with an energy of 5 mJ.

The cavity of the Nd^{3+}:YAG laser (Fig. 3b) consisted of a highly reflecting plane mirror and an output mirror with the curvature radius $r = 3$ m and with the reflection coefficient $R = 87\%$. Both mirrors were highly transmissive at the wavelength $\lambda = 1080$ nm. The cavity was 43 cm long. The passive switch had an initial transmission of 57% and was located between a plane mirror and the active element $\varnothing 6 \times 60$ mm. The focusing parameter $A_g/A_a \sim 1$. The pulses generated were 90 ns long (Fig. 3b) and had an energy of about 1 mJ.

Q switching of the erbium glass laser was realised in the cavity formed by a highly reflecting mirror with the curvature radius $r = 20$ cm and a plane output mirror with the reflection coefficient $R = 90\%$ at the emission wavelength (Fig. 3c). The cavity was 18 cm long and the active element had the size $\varnothing 3 \times 50$ mm. The passive switch had an initial transmission ~ 70%. Q switching was observed for the intracavity focusing parameter $A_g/A_a = 2.8$. The pulses were 60 ns long (Fig. 3c) and had an energy of about 0.3 mJ.

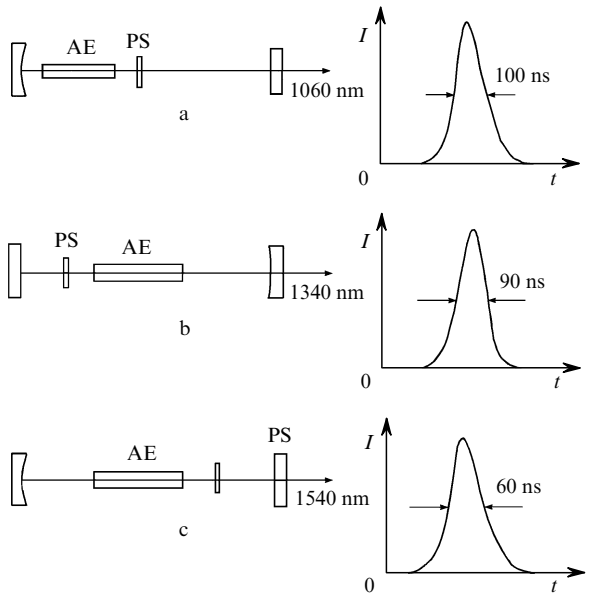

Figure 3. Schematic diagrams of cavities and time profiles of output pulses for YAG : Nd^{3+} (a), $YAlO_3$: Nd^{3+} (b), and Er^{3+} glass (c) lasers with passive Q switching.

In the absence of irradiation, the optical characteristics of passive switches made of glass doped with Cu_2Se ONPs remain stable for 2 to 3 years. The operation life exceeded 10^5 laser shots while the optical strength was about 50 MW cm^{-2} in the case of nanosecond pulses. This value was determined not so much by the optical strength of the glass matrix as by photo-discoloration of the centres absorbing in the infrared. It should, however, be noted that the absorption capabilities of the passive switch are restored completely after one or two hours of heating at the temperature $\sim$900 °C.

A comparatively longer duration of single pulses obtained can be explained by the relatively lower contrast (i.e., the ratio of optical densities in the initial and transparent states), which is equal to 2.5 – 3 and by the optical strength of the passive switches studied. One may expect that the optimisation of preparation technique for glass doped with Cu_2Se ONPs would improve the contrast and optical strength of the passive switches. Application of antireflection coating to the surface of the passive switch together with optimisation of its initial transmission and the reflection coefficient of the output mirror for each of the lasers would substantially raise the energy and reduce the duration of single pulses.

4. Conclusion

Nonlinear optical properties of glasses doped with Cu_2Se ONPs by using sol – gel processing technology have been investigated. An additional wide absorption band with maximum at $\lambda \sim 1000$ nm caused by oxidised nanoparticles and bleached by laser radiation makes it possible to use such glasses as passive switches for solid-state lasers in the near infrared. A passive Q switching regime has been realised for Nd^{3+}:YAG ($\lambda = 1060$ nm) and Nd^{3+}:$YAlO_3$ (1340 nm) lasers, as well as of an Er^{3+} (1540 nm) glass laser by using the glass doped with oxidised nanoparticles of copper selenide.

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