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The Effect of the Relative Position of the Bandgap with Respect to Laser Wavelength on the Behaviour of DFWM in Semiconductor-Doped Glasses

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Abstract. Degenerated four-wave mixing (DFWM) was realised in five commercial semiconductor-doped glasses (Corning CS 3–66, CS 3–67, CS 3–68, CS 3–69, CS 3–70). The reflectivity obtained for each glass seems very dependent on the energy excess ($\delta E = h\nu - E_g$) and relatively independant on αl, the product of the absorption coefficient (α) by the sample thickness (l). The decay time of the DFWM signal was measured for each glass. The relaxation was found to be different when the photon energy is under or over the gap.

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Semiconductor-doped glasses are being extensively investigated [1–16] due to their interesting optical properties first noticed by Jain and Lind [1], who reported a large non-linearity ($\approx 10^{-8}$ esu) associated with a fast response time. Degenerated four-wave mixing (DFWM) experiments performed in glasses containing CdS_xSe_{1-x} microcrystals have provided information about the amplitude of the nonlinearity and on its phase and frequency dependence [2]. Recently, high-order nonlinearities measurements have also been reported in that type of materials [3].

The temporal behaviour of the nonlinearity has been investigated by several groups using different methods yielding rather different results. Similarly to Jain and Lind, Yao et al. observed a fast response time for the DFWM, not resolved by the 30 ns laser pulsewidth [4]. However, such a fast nonlinearity was not observed by Roussignol et al. [5]. They explained the discrepancy between their nanosecond response and the other fast response times by the presence of a permanent photochemical change induced in the doped glass at high fluences which leads to a faster response time [6]. In his paper, Cotter [7] reports fast DFWM signal decay times (10 ps to 50 ns) for pump fluences varying respectively from 55 to 0.5 $\mu J/cm^2$. Subpicosecond band filling and intensity-dependant electron-hole recombination time have also been reported by other techniques [8–9].

This paper reports observations made on five commercial semiconductor-doped glasses (Corning CS 3–66, CS 3–67, CS 3–68, CS 3–69, CS 3–70) using DFWM at high fluences. The incident photon energy (2.33 eV) was higher than the estimated bandgap for filters CS 3–66 and CS 3–67, while it lied under or close to the gap for filters CS 3–68, CS 3–69, and CS 3–70. The reflectivity obtained for each glass is analysed in terms of $\delta E = h\nu - E_g$, the energy excess and seems to be independent on the product of the absorption coefficient (α) by the sample thickness (l). The decay time of the DFWM signal was measured for each glass. The relaxation was found to be different when the photon energy is under or over the gap.

1. Experiments

The conventional ring DFWM setup [17] used for our phase conjugated experiments is depicted in Fig. 1. The input pulse (15 ps and 10 mJ) was selected from a

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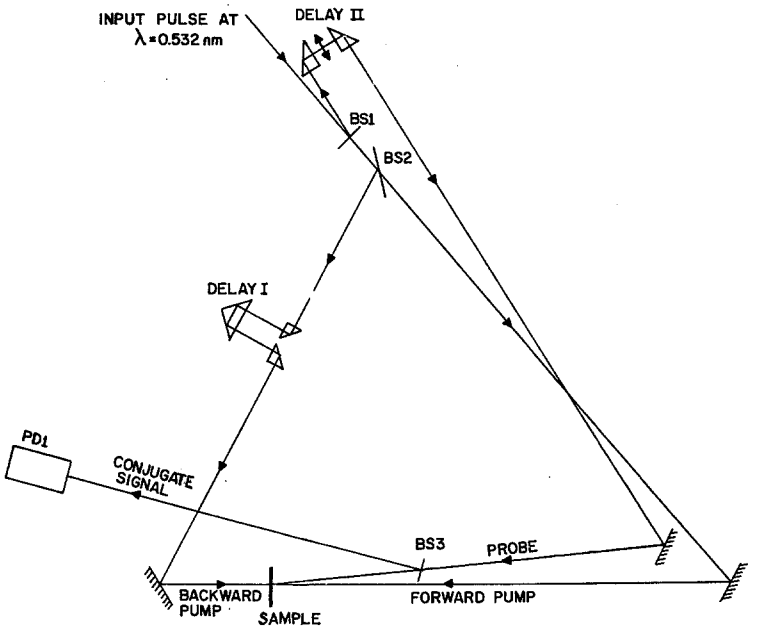

Fig. 1. Experimental setup

mode-locked train delivered by a frequency doubled Nd^+:YAG laser (Quantel YG471) operating at a repetition rate of 5 Hz (532 nm). The angle between the forward pump and the probe was kept at 6°. At the sample position, a few diffraction rings may be observed within the beam diameter which was of the order of 8 mm. The delay between each of the three incoming pulses could be modified by means of two variable delay lines. All the three beams had the same linear polarization and the measurements were performed at room temperature.

The semiconductor-doped glasses studied were commercial filters. The Corning CS3–66 and CS3–67 were 2 mm thick while the CS3–68, CS3–69, and CS3–70 were 3 mm thick. The band gap of these colored filters was determined by the method described by Bube [18]. The linear relation between the square root of the absorption coefficient and the photon energy (Fig. 2) is consistent with an indirect bandgap transition and the values obtained are listed in Table 1.

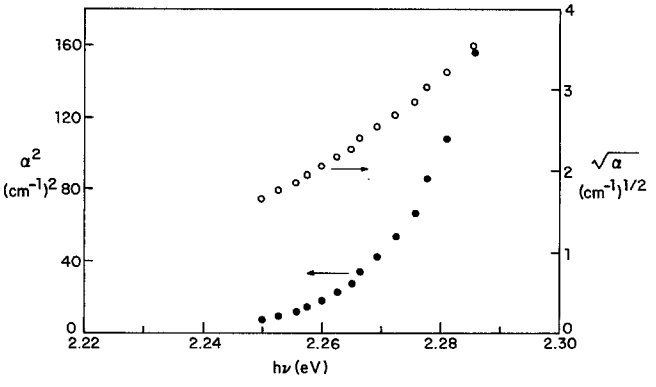

Fig. 2. Evaluation of the bandgap for filter CS3–67

Table 1. Summary of results

Filter	Bandgap [eV]	αl (=532 mn)	m
CS3–66	2.15	>7	3.9
CS3–67	2.22	>7	2.9
CS3–68	2.28	1.60	3
CS3–69	2.33	0.25	2.3
CS3–70	2.37	0.25	2.5

2. Results and Discussion

2.1. The Nonlinearity

As the experiments were performed at high intensities, particular attention has been paid to avoid laser-induced permanent photochemical change in the glasses. The samples were exposed to a small number of laser shots and examined cautiously in order to consider the possibility of the darkening effect described by Roussignol et al. [6]. No evidence of this darkening effect was found.

Reflectivity measurements were performed under temporal coincidence conditions (no delay between the interacting beams) for the five glasses subject of our investigation. Figure 3 shows the maximum reflectivity (obtained with $I_1 = 200$ MW/cm^2, $I_2 = 300$ MW/cm^2, and $I_3 = 500$ MW/cm^2) of each glass versus its bandgap energy. The maximum reflectivity was obtained for filter CS3–68 which has a bandgap 0.05 eV lower than the laser photon energy. Considering an indirect

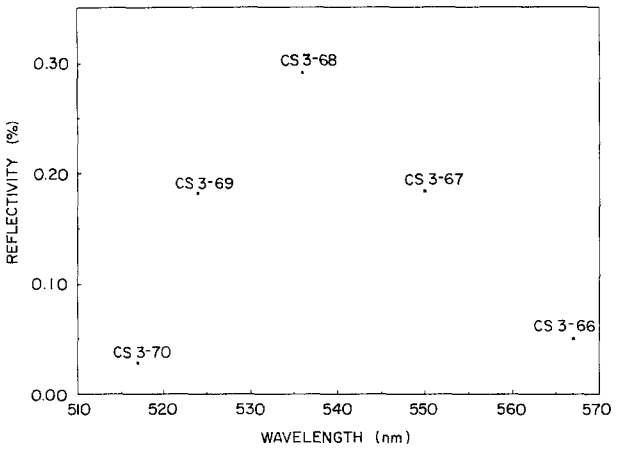

Fig. 3. Maximum reflectivity vs. filter's bandgap energy ($I_1 = 200$ MW/cm^2, $I_2 = 300$ MW/cm^2, and $I_3 = 500$ MW/cm^2)

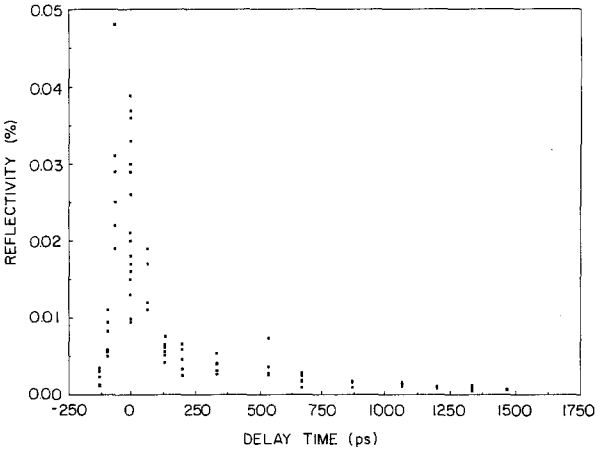

Fig. 5. Reflectivity vs. delay of backward pump for filter CS3–66

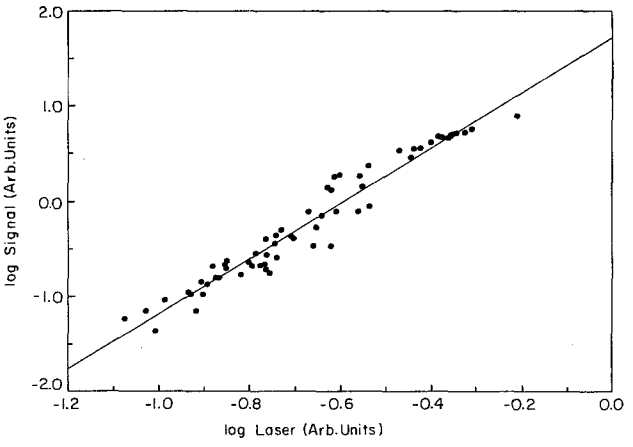

Fig. 4. DFWM signal vs. pump intensity for filter CS3–67

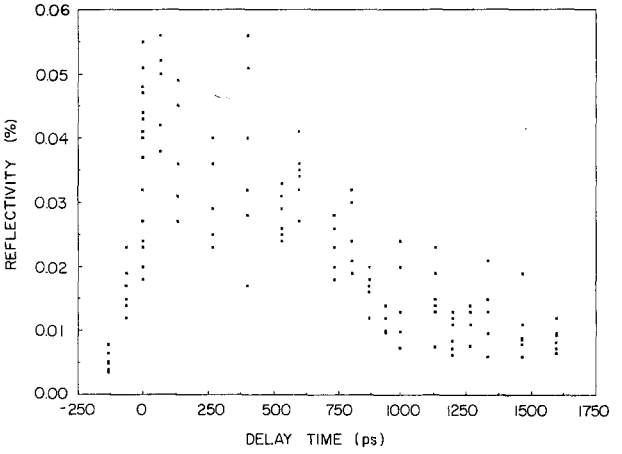

Fig. 6. Reflectivity vs. delay of backward pump for filter CS3–70

transition between the valence and the conduction band, one may obtain a maximum reflectivity when the incident photon energy corresponds to the gap energy plus E_{ac} the energy of the emitted phonon ($h\nu = E_g + E_{ac}$), which is consistent with the expected value of E_{ac} for longitudinal phonon excitation [8].

One may also notice the equivalent reflectivities for filters CS3–67 and CS3–69 and for filters CS3–66 and CS3–70 which have different αl values (Table 1) but have almost equal energy difference from the 2.28 eV where the maximum reflectivity is observed. Furthermore, the two pairs of filters CS3–66 : CS3–67 and CS3–69 : CS3–70 have very different reflectivities even though their αl value is about the same. However, one has to notice that filters CS3–66 and CS3–67 are 2 mm thick while CS3–69 and CS3–70 are 3 mm thick in order to compensate for higher absorption.

The dependence of the signal intensity on the incident laser intensity has been investigated for each semiconductor-doped glass. Figure 4 shows a typical log-log plot of that dependence (corresponding to filter CS3–67 in that specific case). The slope obtained here is consistent with an unsaturated process. For the five glasses studied, the slopes measured vary from 2.3 to 3.9 (Table 1). A slope lower than 3 is attributable to saturation effects while the value of 3.9 indicates the contribution of a higher order non-linear process [19].

2.2. *Temporal Behaviour*

The temporal behaviour of the DFWM has been investigated by means of reflectivity measurements as a function of the delay of the backward pump. Figures 5 and 6 show the two typical time response behaviours obtained. Figure 5 shows a fast response time (100 ps) which corresponds to the typical temporal response of filters CS3–66 and CS3–67. For those filters, the excitation energy ($h\nu$) is higher than the estimated bandgap. For filters CS3–68, CS3–69, and CS3–70, where $h\nu \leqq E_g$, the temporal behaviour corresponds to the one shown in Fig. 6 and is characterized by an important longlife contribution (several nanoseconds) underlying a fast process (similar to the one observed in filters CS3–66 and CS3–67). This slow effect may be attributed to electron-hole recombination.

The shortening of the response time of the nonlinearity for filters CS3–66 and CS3–67 ($h\nu \geqq E_g$) may be explained by the energy excess which reduces drastically the electron-hole recombination time [8]. The thermal effect is not expected to be seen here since the associated risetime is larger than 1 ns [20].

3. Conclusion

DFWM has been realized in Corning CS3–66, CS3–67, CS3–68, CS3–69, and CS3–70 semiconductor-doped glasses. The maximum reflectivity has been demonstrated to be very dependant on δE and relatively independant on αl. The temporal behaviour of the nonlinearity has been seen to depend on the sign of δE. It has been demonstrated that it is possible to shorten the response time of the nonlinearity of semiconductor-doped glasses by working at an incident photon energy higher than the bandgap. However, the choice of the incident wavelength is limited by the absorption losses.

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