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BRILLOUIN SCATTERING OF GLASSES DOPED WITH SEMICONDUCTORS CdS_xSe_{1-x}

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Brillouin scattering of glasses doped with semiconductors CdS_xSe_{1-x} (cut filters ;Y44 for x = 1 and O56 for x= 0.26) were performed. The size effects of microcrystals were investigated on the velocities of longitudinal acoustic phonons in the glasses with various annealing times (t_a) and temperatures (T_a). The sizes of microcrystals in not Y44, but O56 samples were determined for radii larger than 2nm by photoacoustic measurements. Main results obtained were followed: 1) Brillouin shifts ($\Delta \nu$) of any annealing samples decreased a little bit, but clearly in comparison with those of no-annealing samples, 2) no size effect of microcrystallite radii larger than 2.5 nm were observed, and 3) $\Delta \nu$ in the glasses with t_a =0 for any T_a were the minimum. The causes of above results will be considered.

1. INTRODUTION

The semiconductors CdS_xSe_{1-x} -doped glasses (SDG) are commercially available in the form of yellow-to-red sharp-cut filters. These glasses as nonlinear optical materials[1-3] have been actively studied with emphasis on quantum confinement effects[4] exhibited at small crystallite size. The semiconductors CdS_xSe_{1-x} crystallites embedded in the glass matrix are thermally developed. The quantum size effects are mainly indicated by optical methods; photoluminescence[5-7], absorption[6,8-10], emission[8] and photoacoustic spectra[11-16], etc. These quantum size effects have been investigated by naturally focusing experimental and theoretical attention on the CdS_xSe_{1-x} microcrystal.

In this paper, we have directed the attention to not CdS_xSe_{1-x} microcrystals inside the glass, but the glass itself containing various sizes of CdS_xSe_{1-x} microcrystals. Brillouin scattering of SDG have been performed varying the thermal treatments of annealing times (t_a) and annealing temperatures (T_a). We studied two kinds of glasses containing CdS_xSe_{1-x} crystallites: HOYA glass Y44 for x=1 and HOYA O56 for x=0.26.

2. EXPERIMENTS

The Ar ion laser with a longitudinal single mode was used as a light source of Brillouin scattering experiment and was operated at 514.5 nm wavelength with an average power of about 50mW. Microscopic Brillouin spectra[17] were obtained in a backward scattering geometry using a 3-3 pass tandem Fabry-Perot interferometer (Sandercock type). We assigned 1000 channels for each spectrum scanned for 10s. Each scan was repeated 30 times. Scattered light was detected

	Y44	O56
SiO_2	6.1	51.7
B_2O_2	3.9	3.9
Al_2O_3		
Na_2O	1.0	
K_2O	18.6	22.5
MgO		
CaO	13.8	
BaO		
ZnO		19.5
PbO		
As_2O_3		
KHF_2		
CdS	0.6	1.7
S	0.5	0.15
Na_2SeO_3		
CdS_xSe_{1-x}	x = 1	x = 0.26

Table I Composition of HOYA "sharp-cut" filter glasses.

using a photomultiplier (Hamamatsu R943-02). The photopulses were counted by a photon counter (Princeton model 1120-1109) and accumulated in a personal computor (PC-9801DA).

The composition of the base glass used for Y44 and O56 are shown in Table I with wt%. Note that there are considerable deference for the composition of the base glass between two samples, Y44 and O56.

The sizes of CdS_xSe_{1-x} microcrystal in the glass were examined with photoacoustic measurements (PAS) by Q. Shen and T. Toyoda in authors. However, Y44(x=1) sample was not available due to incorporation of zinc[5].

3. RESULTS and DISCUSSION

In general, the higher the annealing temperature T_a and the longer the annealing time t_a, the larger the average crystallite size[10,18] and the larger the number density of particles. Brillouin scattering have been carried out for two samples Y44 and O56 with various heat-treatments in term of T_a and t_a. Brillouin spectra of longitudinal acoustic phonons in Y44 sample are shown in Fig.1 as a parameter of T_a for t_a = 0 and 60min. It was certainly found that the peaks of Brillouin spectra of longitudinal acoustic phonon between the samples without and with heat-treatments indicated slight but clear difference.

One example for annealing time dependence of Brillouin shifts ($\nabla \nu$) in Y44 samples is shown in Fig.2 for the case of T_a = 550 ° C. The $\nabla \nu$ for unannealing sample was the maximum, however, it was the minimum for t_a = 0 and increased a saturated value quickly with making t_a longer. Here, the heat treatment of t_a = 0 means heating the sample till T_a in the oven and taking it away from the oven as soon as the temperature reached at T_a. Also, It is noted that the unannealing samples have been already received some heat-treatment since they are sold as commercial sharp cut-filter. Therefore, the sizes of CdS_xSe_{1-x} microcrystal in the unannealing samples ought to be grown to some degree though the history of heat-treatments is unknown.

The $\nabla \nu$ of Y44 sample are shown as a function of T_a for t_a = 0, 60 and 120 min in Fig.3 together with unannealing result. The following results were obtained: 1) $\nabla \nu$ decreased gradually from T_a = 500 to 650℃ 2) $\nabla \nu$ showed the minimum value above 650℃. 3) the difference of $\nabla \nu$ on annealing times were the maximum at 550℃ and most negligible above

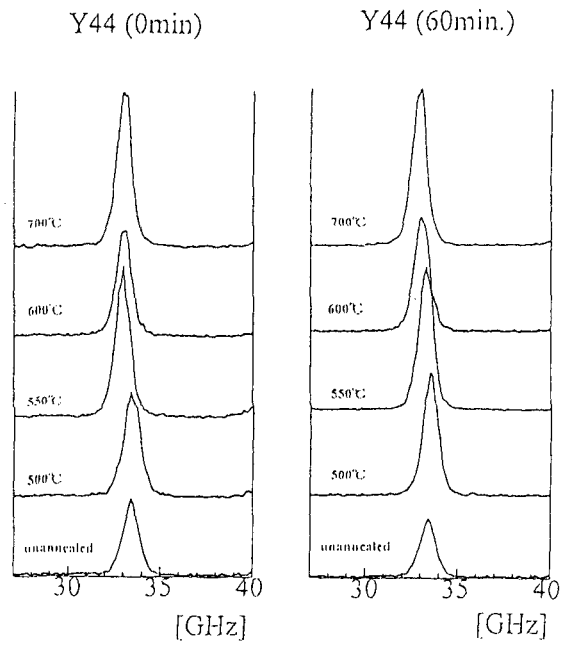

Fig.1 Brillouin spectra of Y44 samples at various annealing temperatures for annealing times, 0 min and 60 min.

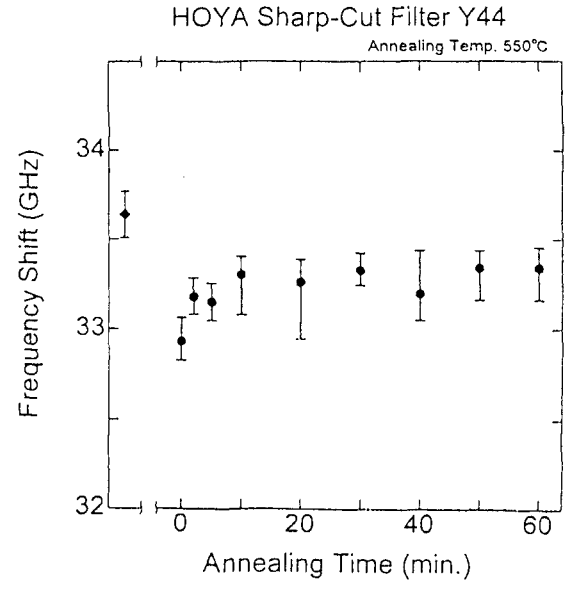

Fig.2 Annealing time-dependence of frequency shift of Brillouin peaks in Y44 samples at annealing temperature ,550℃.

650 ℃. The variation of $\nabla\nu$ for any heat treatments was not large but clear. What do these results mean? Similar measurement for O56 sample to be able to estimate the sizes of crystallite have been performed as shown in Fig.4. There are almost no discrepancy between results of Y44 and O56 samples , though the $\nabla\nu$ -values of O56 scattered a little more than these of Y44 due to absorption of incident light

It was found from PAS[19] that the microcrystal did not create below about 650℃ even with increasing t_a and remained the radii of microcrystals in the neighborhood of 2.5nm. Therefore, above all results in term of O56 are again drawn as a function of average radii (r_{av}) of microcrystal in the glass matrix in Fig.5. In result, 1) $\nabla\nu$ for unannealing samples differed a little bit, but clearly, from $\nabla\nu$ for annealing one. 2) $\nabla\nu$ of t_a= 0-samples for any T_a went down the minimum values, though the microcrystals kept the size constant probably. 3) $\nabla\nu$ did not change regardless of radius-variation by annealing the samples from 0 to 120 minute at T_a=700℃.

Although the estimation of microcrystal-size by PAS was scattered considerably, it was certain that the sizes changed for t_a > 10min at 700℃. Above result of 3) showed no size-dependence of $\nabla\nu$ for r_{av} > 2.5nm. Then, the causes of results of 1) and 2), must be considered. First, the glass itself became to be stress-free by annealing it even a little since the internal stress might remain in the glass due to rapid-cooling of batch melted above 1000 ℃. Second, although the average sizes did not change, it can be supposed there are certainly something to happen actively inside the glass during one heat-cycle between room temperature and T_a. At the present stage, it was imaged that the diffusive decomposition and recondensation growth of many atoms or molecules, and then, dissolution and growth of cluster or microcrystal etc. occur probably.

Main results obtained are summarized in Table II in term of averaged radius of microcrystal, frequency shift of Brillouin spectra and relative velocity of longitudinal acoustic phonon. Here, velocity v_0 represents one of unannealing sample. Taking into account the a few % rate of doping semiconductors CdS_xSe_{1-x} in the glass, the results of frequency shift-variation and relative velocity are reasonable.

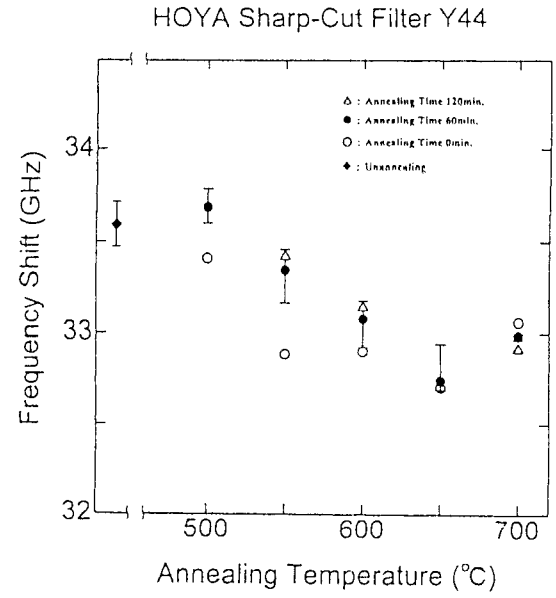

Fig.3 Annealing temperature-dependence of Brillouin frequency shifts in Y44 samples as a parameter of annealing times, 0, 60 and 120 min.

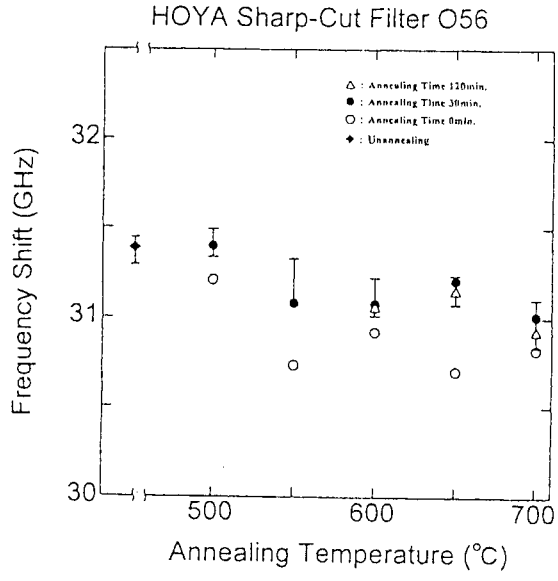

Fig.4 Annealing temperature-dependence of Brillouin frequency shifts in O56 samples as a parameter of annealing times, 0, 60 and 120 min.

4 CONCLUSION

Brillouin scattering of SDG with various heat-treatments have been performed. Brillouin shifts between the samples without and with heat-treatments indicated slight but clear difference. The glass became soft a little by annealing. However, no quantum size effects were yet observed by Brillouin scattering. The causes of obtained results are unclear. Further investigation will need continuing.

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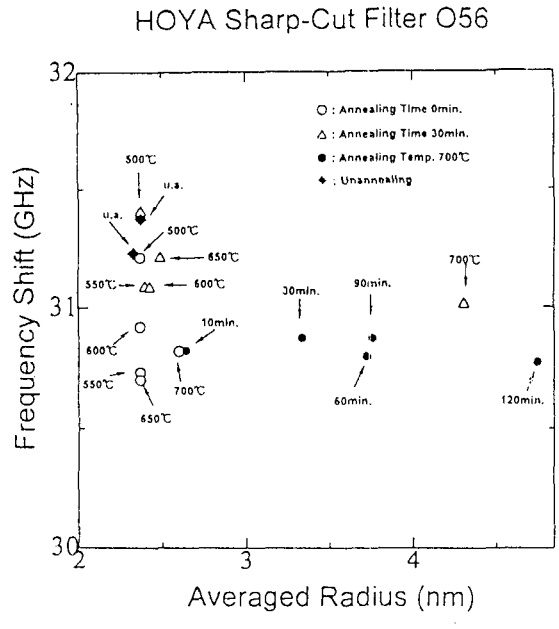

Fig.5 Averaged radius-dependence of Brillouin frequency shifts in O56 for various annealing times and temperatures.

	Y44			O56		
	Un-annealing	550℃ 0min.	700℃ 60min.	Un-annealing	550℃ 0min.	700℃ 30min.
Averaged Radius [nm]	*	*	*	2.37	2.40	4.31
Frequency Shift [GHz]	33.47	32.89	32.99	31.39	30.73	31.01
$\frac{\upsilon_0-\upsilon}{\upsilon_0}$	*	1.71×10^{-2}	1.44×10^{-2}	*	2.08×10^{-2}	1.20×10^{-2}

Table II Summary

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