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Comparison of photodarkening in CdS_xSe_{1-x}-doped and CdS-doped glasses

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Optical properties of semiconductor-doped glasses have been investigated extensively, since these materials have large optical nonlinearity with a fast response time. Roussignol *et al.* [1] reported that the response time of nonlinear signal and luminescence of CdS_xSe_{1-x}-doped glass decreased by light irradiation. This photoinduced irreversible process is called photodarkening. The photodarkening has been investigated mainly in CdS_xSe_{1-x}-doped glasses [1–3]. On the other hand, we have investigated photodarkening mainly in CdS-doped glasses of Toshiba using electron spin resonance (ESR) [4–6]. In the early years of our investigation about semiconductor-doped glasses, we investigated photodarkening in CdS_xSe_{1-x}-doped glass, Toshiba Y-51, using ESR [7, 8]. However, change in ESR spectrum is not so large in CdS_xSe_{1-x}-doped glasses, since ESR signal is observed in this glass before light irradiation. On the contrary, ESR signal is very weak in CdS-doped glasses before irradiation. Thus, we have investigated photodarkening mainly in CdS-doped glasses of Toshiba. On the other hand, Yanagawa and Nakano observed photoinduced ESR signal in CdS_xSe_{1-x}-doped glass, Hoya O-54 [9]. They observed three ESR signals with $g = 1.990$, 1.999 and 2.010. The signal at $g = 1.990$ is large and similar to our results for CdS-doped glasses [4–6]. On the contrary, the signal at $g = 2.010$ is small and different from our results [4–6]. Since manufacturer of sample, composition of semiconductor and laser used by Yanagawa and Nakano [9] are different from those used by us, we have carried out comparative study about photodarkening in CdS_xSe_{1-x}-doped and CdS-doped glasses.

The sample mainly investigated was CdS_xSe_{1-x}-doped commercial filter glass (Hoya O-54) of about 2.5 mm thickness. Concentration of CdS_xSe_{1-x} is about 0.5 wt%. The composition of CdS_xSe_{1-x} nanocrystals was determined to be $x = 0.42$ from Raman spectrum [10]. The glass composition was analyzed by an electron probe microanalyzer (EPMA; Kevex Delta II). These glasses were exposed to pulsed light from an N_2 laser (Usho YKN-900; wavelength = 337.1 nm, pulse duration = 5 ns, peak intensity = 5 MW/cm^2, repetition rate = 1 Hz) for 4 min or X-ray from an X-ray diffractometer (Rigaku CN4057A2; Cu target, 35 kV, 20 mA) for 10 min at 300 K. Penetration depth of laser light is less than 0.2 mm. The irradiated glass was annealed in air at 200°C and 400°C for 2 h.

Transient characteristics of luminescence were measured at 300 K using another N_2

laser (Laser Photonics LN120; wavelength = 337.1 nm, pulse duration = 0.3 ns, repetition rate = 7 Hz) and an optical multichannel analyzer with a gate (Princeton Instruments D/SIDA-700) [4–6]. The minimum gate time was 5 ns. The ESR spectra were measured at 77 K using an X-band spectrometer (JES FE-1X). The g-values of the signals were determined using a MgO:Mn marker.

A luminescence band with a peak at about 530 nm is observed in CdS_xSe_{1-x}-doped glass, O-54, at 300 K. This band is attributable to the band-to-band type or shallow-trapping state-to-band-type transition [11]. Noticeable change in the specraral shape of luminescence is not observed after irradiation and thermal annealing. On the other hand, luminescence intensity decreases after irradiation and partly recovers after annealing. This result is similar to those of CdS-doped glasses [4–6]. Fig.1

Transient characteristics of luminescence also change after irradiation and annealing. Fig. 1 shows transient characteristics of luminescence from O-54 at peak wavelength. Intensities at $t = 0$ ns are normalized. The decay rate of luminescence from O-54 after laser irradiation is faster than that before irradiation. The decay rate of luminescence almost recovers its initial value after annealing at 400°C. On the contrary, the decay rate partly recovers after annealing at 200°C. This result is similar to those of CdS-doped glasses of Toshiba [4–6] and Hoya Y-44. However, change in the decay rate in CdS_xSe_{1-x}-doped glass is smaller than those in CdS-doped glasses.

We measured decay rate of luminescence from Hoya Y-44 and O-54 as a function of irradiation time. The decay rate increases with increasing irradiation time, and then saturates at about 10 min. This result is similar to that in CdS-doped glasses, Toshiba Y-44 and Y-45 [6]. Fig.2

ESR spectra were measured to investigate the nature of photoinduced defects. Fig. 2 shows ESR spectra of CdS_xSe_{1-x}-doped glass, O-54, at 77 K. ESR signals are observed before laser irradiation. Additional ESR signals appear after irradiation. The ESR signal at about $g = 1.99$ is considered to be due to electron traps in glass, since this signal is observed after X-ray irradiation. This signal disappears after annealing at 200°C. However, the decay rate of luminescence only partly recovers after annealing. Moreover, the decay rate of luminescence from the X-ray irradiated sample, which shows large ESR

signal at about $g = 1.99$, is the same as that from the sample before irradiation. Thus, the electron traps do not play important role in change in the luminescence properties. Fig.3

The signal at about $g = 2.01$ does not show noticeable change after irradiation. On the contrary, photoinduced signal near $g = 2.01$ is observed in CdS-doped glasses after irradiation as shown in Fig. 3 (Hoya Y-44), and this signal is considered to be due to photoinduced defects in the interface region between CdS nanocrystals and the glass matrix [4–6]. The intensity of the photoinduced signal near $g = 2.01$ is almost the same as that of $g = 1.99$ in CdS-doped glasses. The additional signal near $g = 2.01$ disappears after annealing at 400°C. The spectral shape after annealing at 400°C is the same as that before irradiation. Simultaneously, the decay rate of luminescence recovers its initial value after annealing. Thus, the photoinduced defects are considered to act as nonradiative recombination centers, which are related with the photodarkening. The signal at about $g = 2.01$ in CdS_xSe_{1-x}-doped glass, O-54, before irradiation may be due to other defects. This signal is very weak in CdS-doped glasses of Toshiba [4–6]. These results indicate that number of defects are relatively few in CdS-doped glass of Toshiba before irradiation and defects are created by irradiation, since ESR signal is relatively weak before irradiation and increases after irradiation. On the other hand, CdS_xSe_{1-x}-doped glass of Hoya may contain many defects before irradiation. So that we cannot observe effect of irradiation on ESR signal near $g = 2.01$ in CdS_xSe_{1-x}-doped glass. Similar results were observed in another CdS_xSe_{1-x}-doped glass ($x = 0.58$), Hoya Y-52.

Photoinduced changes in luminescence intensity, decay rate of luminescence and photoinduced signal of ESR near $g = 2.01$ in CdS-doped glasses are larger than those in CdS_xSe_{1-x}-doped glass. These results indicate that photodarkening occurs easier in CdS-doped glasses than in CdS_xSe_{1-x}-doped glasses. We consider that photoexcited carriers in CdS nanocrystals have higher energy than those in CdS_xSe_{1-x} nanocrystals, since bandgap of CdS is larger than that of CdS_xSe_{1-x}. So that carriers may escape easier from CdS than CdS_xSe_{1-x} nanocrystals.

Yanagawa and Nakano [9] have reported ESR spectrum of CdS_xSe_{1-x}-doped glass, Hoya O-54. They observed three ESR signals with $g = 1.990$, 1.999 and 2.010. The signal at $g = 1.990$ is large and similar to that of the present result shown in Fig. 2. The signal

at $g = 2.010$ is small. This result is consistent with our result, since photoinduced signal at $g = 2.01$ is also small in the present result. They used laser light with wavelength of 532 nm. Thus, photodarkening is considered to be independent of wavelength of light for irradiation, when photon energy is larger than band gap energy of semiconductor. Fig.4

The sample used by Yanagawa and Nakano [9] is nominaly the same as that used in the present experiment. However, the signal near $g = 2.01$ is very weak in the sample used by them. Possible origin of this difference is the difference in glass composition. Glass composition may depend on time of production. So that, we measured glass composition using EPMA. Fig. 4 shows composition of cations in these glasses. This result indicates that the glass composition of the present sample is different from that of Yanagawa and Nakano [9].

In summary, luminescence and ESR spectra of CdS_xSe_{1-x}-doped glass of Hoya were measured before and after laser irradiation and compared with those of CdS-doped glasses of Hoya and Toshiba. The intensity of ESR signal related with the photodarkening in CdS_xSe_{1-x}-doped glass is weaker than those in CdS-doped glasses.

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Figure captions

Fig. 1. Transient characteristics of luminescence from CdS_xSe_{1-x}-doped glass, O-54, at 300 K. Intensities at $t = 0$ ns are normalized. Curves were drawn through data points as guide to the eyes.

Fig. 2. ESR spectra of CdS_xSe_{1-x}-doped glass, O-54, at 77 K.

Fig. 3. ESR spectra of CdS-doped glass, Y-44, at 77 K.

Fig. 4. Composition of cations in glasses, O-54, used in the present investigation and used by Yanagawa and Nakano [9].

Fig. 1

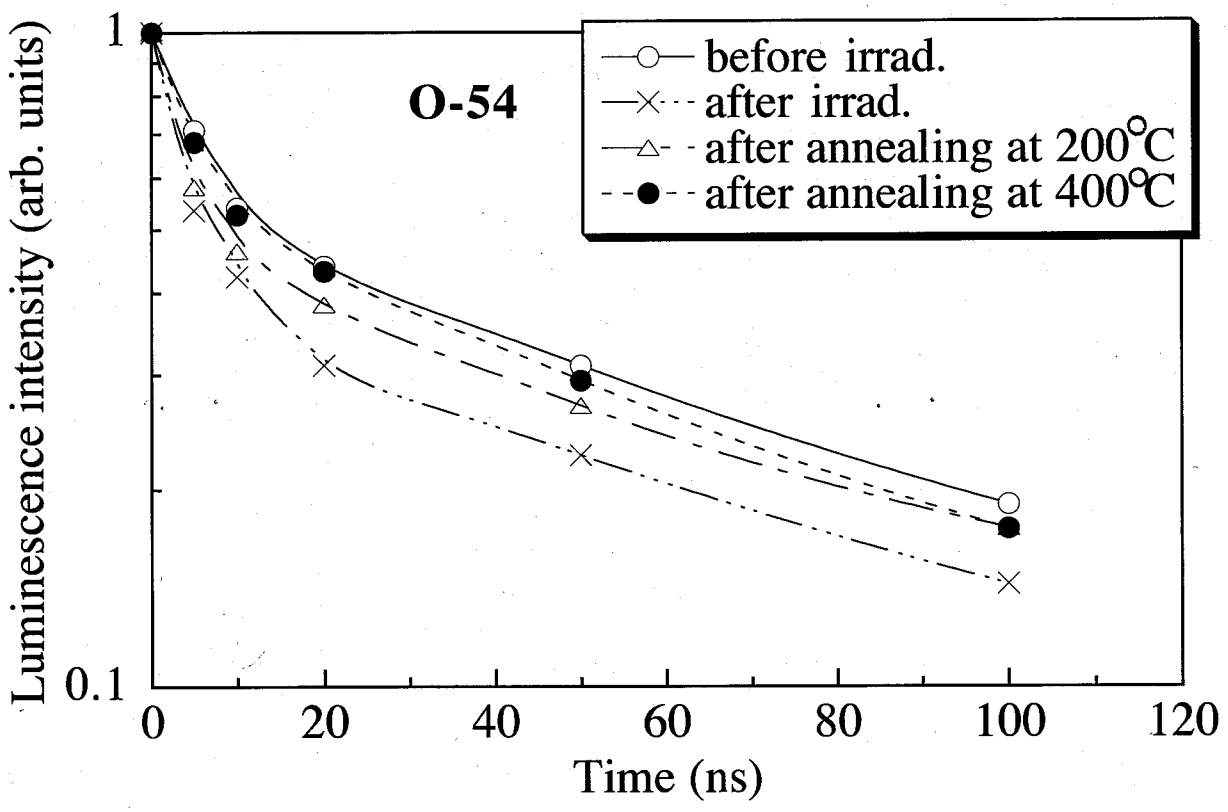

Luminescence intensity (arb. units)
1
0.1
0
20
40
60
80
100
120
Time (ns)
O-54
before irrad.
after irrad.
after annealing at 200°C
after annealing at 400°C

Fig. 2

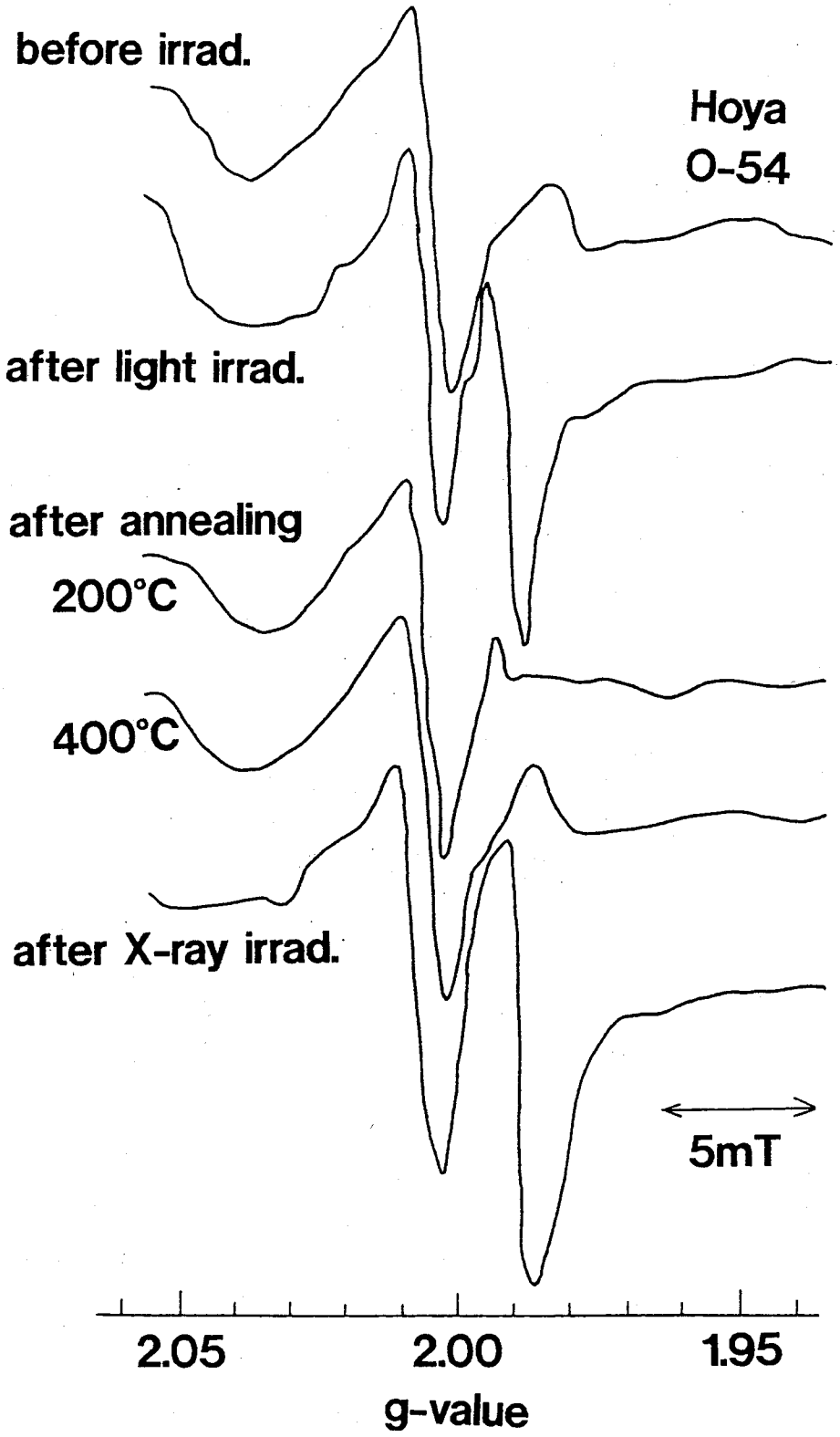

before irrad.
Hoya
O-54
after light irrad.
after annealing
200°C
400°C
after X-ray irrad.
5mT
2.05
2.00
1.95
g-value

Fig. 3

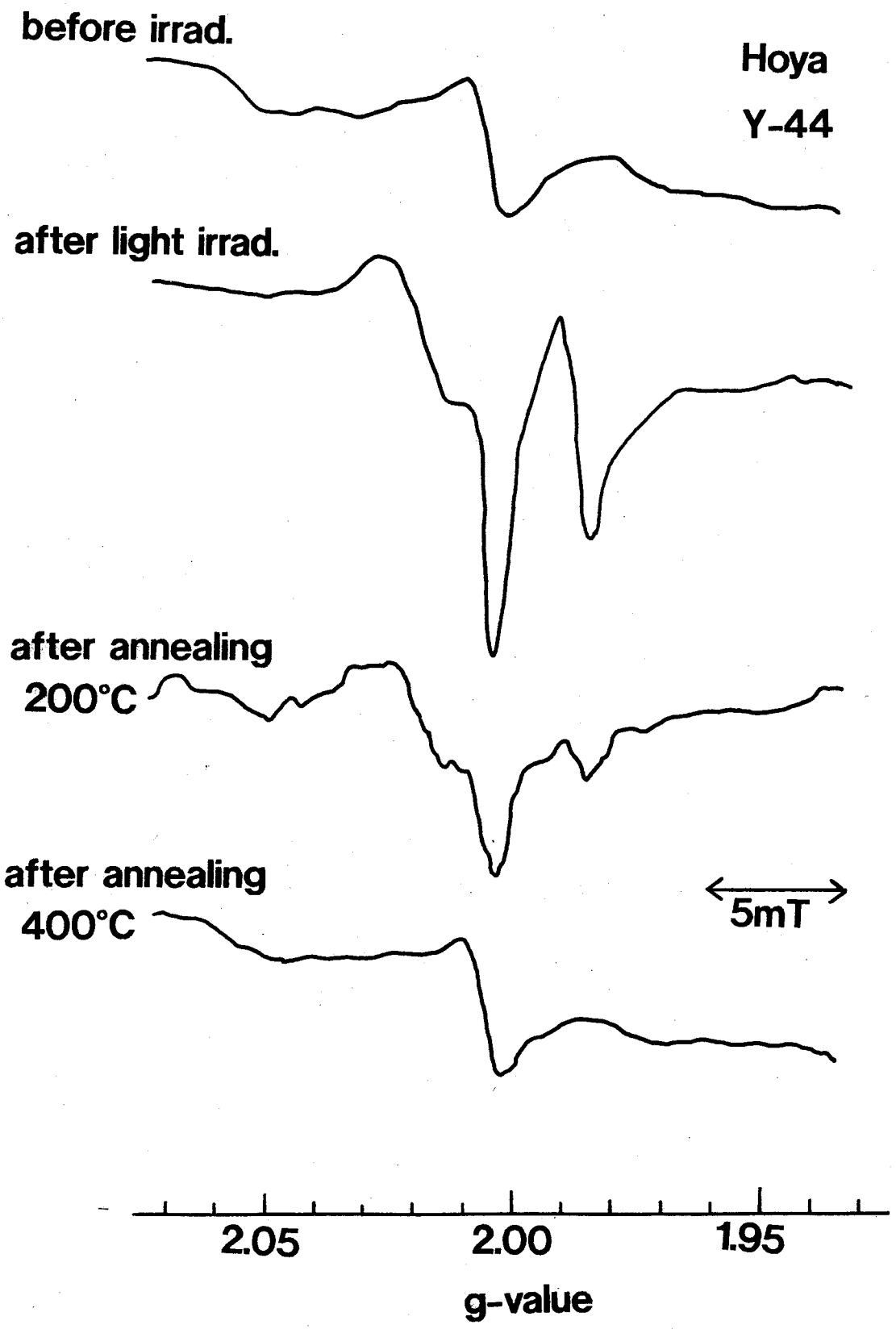
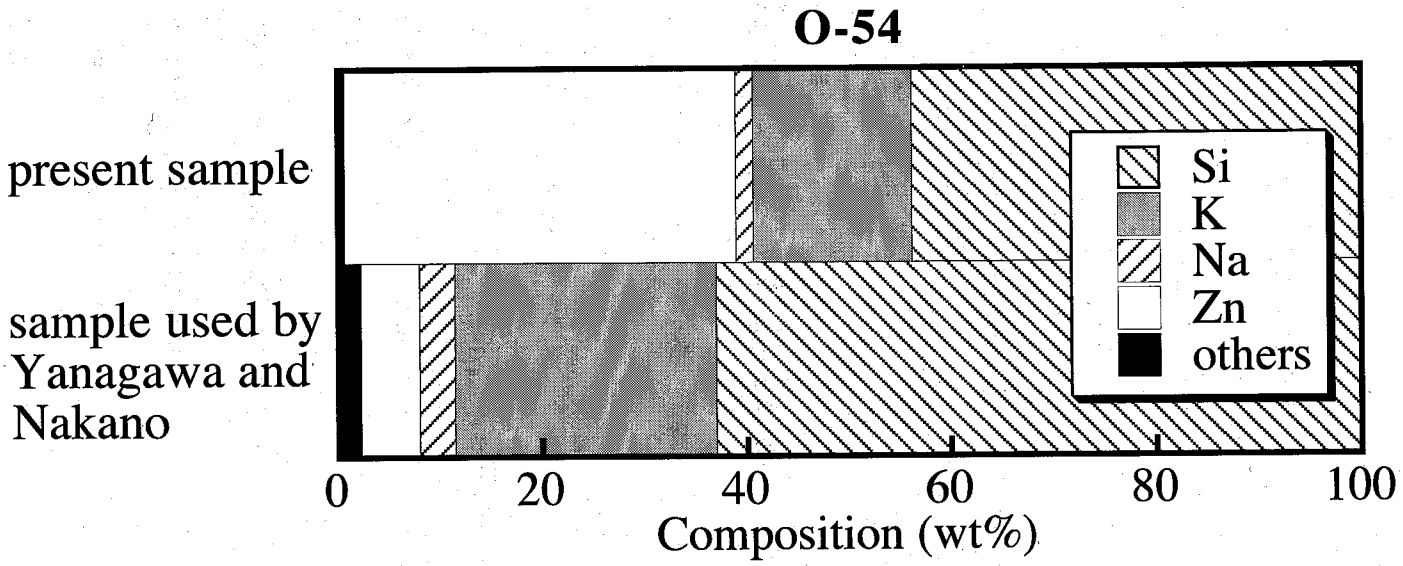

before irrad.
Hoya
Y-44
after light irrad.
after annealing
200°C
after annealing
400°C
5mT
2.05
2.00
1.95
g-value

Fig. 4


O-54
present sample
sample used by Yanagawa and Nakano
Si
K
Na
Zn
others
0
20
40
60
80
100
Composition (wt%)