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Silver-activated radiophotoluminescent glass: band assignments and a novel readout system using a modulated UV laser diode

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Abstract. We investigated the assignments and characteristics of the X-ray-induced colour centres in a silver-activated radiophotoluminescent glass. The induced-absorption spectrum was decomposed into six Gaussian bands, which were, in turn, attributed to the Ag^+, Ag_3^+ or Ag_3^{2+}, Ag_2^+, Ag^{2+}, Ag^0 and hole-trap centres, respectively, by means of optical and thermal measurements. All components of the blue and orange radiophotoluminescence (RPL) in a silver-activated phosphate glass were confirmed to be X-ray-induced colour centres. We also proposed and constructed a new readout system for the measurement of the RPL of the glass dosimeter that considers the characteristics of the radiation-induced bands.

1. Introduction

The silver-activated phosphate glass (designated PG:Ag) after the exposure to ionizing radiation emits an intense radiation-induced orange luminescence by the excitation with a pulsed ultraviolet (UV) laser, which is called radiophotoluminescence (RPL). Such a dose-dependent RPL in PG:Ag has long been examined [1-3] for large-scale use in personal and environmental monitoring of the dose. In particular, radiation-induced colour centres in PG:Ag have been extensively studied by means of optical spectroscopy [1, 3] and the electron spin resonance (ESR) method [2]. When PG:Ag is exposed to ionising radiation, various colour centres such as Ag^0, Ag_2^+, Ag^{2+}, Ag_3^+ and other silver ion species are produced and the existence of each these species has been confirmed by ESR studies [2]. However, the spectral contribution of these small clusters to the overall spectrum remains unknown.

As the basic characteristics of these Ag_m^{X+} centres have been studied, a readout system has been developed for the measurement of the RPL of the glass dosimeter [4-6] based on a time-resolved technique using a pulsed UV nitrogen laser excitation. The basic principle of the conventional reader is as follows [4]: the radiation-induced component (normally, the orange RPL with lifetime values of 2 µs < t ≤ 20 µs) is only integrated by subtracting the radiation independent short-term (t ≤ 2 µs) and long-term (t > 20 µs) components of the pre-dose fluorescence from the total RPL values. If these latter terms do not result from parasitic luminescence, then the time-resolved technique will not be necessary to discriminate the orange RPL from short- and long-term components. This will eliminate the instabilities of the pulsed laser power, the degradation of the induced colour centres and the complicated processing that is required due to the use of a pulsed UV N_2 laser excitation.

The purpose of this study is to further study the characteristics of the induced colour centres in PG:Ag after exposure to X-rays. In addition, a new reader for the measurement of the RPL of the glass

dosimeter using a modulated continuous-wave (cw) UV laser diode and phase-sensitive method is proposed and constructed. Preliminary results using a home-made reader are also presented.

2. Experimental Details

A commercially available GD-450 dosimeter (AGC Techno Glass) was used as the radiophotoluminescent PG:Ag. Samples were cut from the original glass dosimeter plate to a size of approximately 10 mm × 7 mm × 1 mm. The weight composition of the GD-450 dosimeter was 31.55% P, 51.16% O, 6.12% Al, 11.00% Na and 0.17% Ag.

All samples were coloured by irradiation from an X-ray unit (energy: 8 keV) with a copper target operated at 30 kV and 20 mA. In this work, the samples were irradiated such that the absorbed doses ranged from 30 mGy to 24.5 Gy. Absorption, excitation and emission measurements were performed at room temperature using a Hitachi U-2010 UV-VIS and an F-2500 fluorescence spectrophotometer. Radiative lifetime measurements were performed using a time-resolved spectrofluorometer (Horiba, NAES-1100) with a resolution limit of sub-ns, which was operated based on the time-correlated multi-photon counting technique [7].

For the direct photo-induced reduction from Ag^+ ions to Ag^0 centres in PG:Ag, this work used a regeneratively amplified 800-nm Ti:sapphire laser (Coherent, Mira and RegA) that emitted 80-fs, 250-kHz mode-locked pulses. The femtosecond (fs) laser pulses were focused using a 20× objective lens (NA=0.40) to a depth of 250 μm beneath the sample surface with the help of a computer-controlled 3D X-Y-Z stage at a speed of 1000 and 50 μm/s. The pulse energy ranged from 2.0 to 3.0 μJ/pulse and the spot diameter was approximately 2 μm.

3. Results and Discussion

3.1 Optical characteristics and peak fitting analysis

Figure 1(a) shows the absorption spectrum (solid line) of the X-ray-irradiated PG:Ag under an absorbed dose of 24.5 Gy, and its spectrum was decomposed into the sum of separate Gaussian bands (indicated by a dotted line). The peak fitting analysis was carried out on the basis of the strong analogy with X-ray-irradiated silver-activated sodium chloride (NaC:Ag) [8]. In the case of NaCl:Ag, the appropriate absorption band could be decomposed into six bands (not shown here) with peaks at 224, 276, 308, 335, 382 and 443 nm, which are called the "A", "B", "C", "D", "E" and "F" bands, respectively. The peak positions of each band are in good agreement with those of the observed radiation-induced bands in NaCl:Ag [9,10]. The absorption peaks of the RPL in NaCl:Ag are mainly attributed to bands "B", "C" and "D". The origin of these bands in NaCl:Ag has already been clarified as follows: bands "B" and "D" are related to F (i.e., a single electron trapped at an anion vacancy) and F_2 (i.e., a pair of nearest-neighbour F centres along a <110> axis) centres with neighbouring Ag^+, respectively, and the narrow "C" band is strongly related to the Ag^0 centres located at large lattice defects. In the case of PG:Ag, the absorption bands could also be decomposed into six absorption bands from "A" to "F", with peaks at 225, 252, 270, 307, 354 and 424 nm, respectively.

Figure 1 (b) shows the excitation spectra (Curves 1 and 2) and the corresponding emission spectra (Curves 3-5) after X-ray irradiation for PG:Ag. An absorption spectrum is also shown for comparison. The excitation spectra consist of two different spectra. One spectrum peaks at 308 nm (Curve 1) for emission at 560 nm, and the other peaks at 270 and 345 nm (Curve 2) for emission at 450 and 560 nm. The former corresponds to the decomposed 307-nm (corresponding to "D") Gaussian band, while the latter mainly corresponds to the decomposed 270- ("C") and 354-nm ("E") bands, respectively. The blue emission and some portion of the orange emission are strongly related to the 270- and 345-nm excitation bands.

3.2 Femtosecond laser exposure

Recently, intense fs laser pulses with high-peak power densities (>100 TW/cm^2) and high repetition rates (>200 kHz) have enabled the direct precipitation of silver nanoparticles in silver-activated

glasses without heat treatment [11]. In the case of silver-activated glasses, it is well known that irradiation with fs laser pulses as well as X-rays and subsequent annealing at high temperature (~770 K) for 30 min bring about the reduction of Ag^+ ions to Ag^0 atoms and result in the formation of plasmonic nanoparticles, as observed using luminescence and ESR spectroscopy and transmission electron microscopy (TEM) [12].
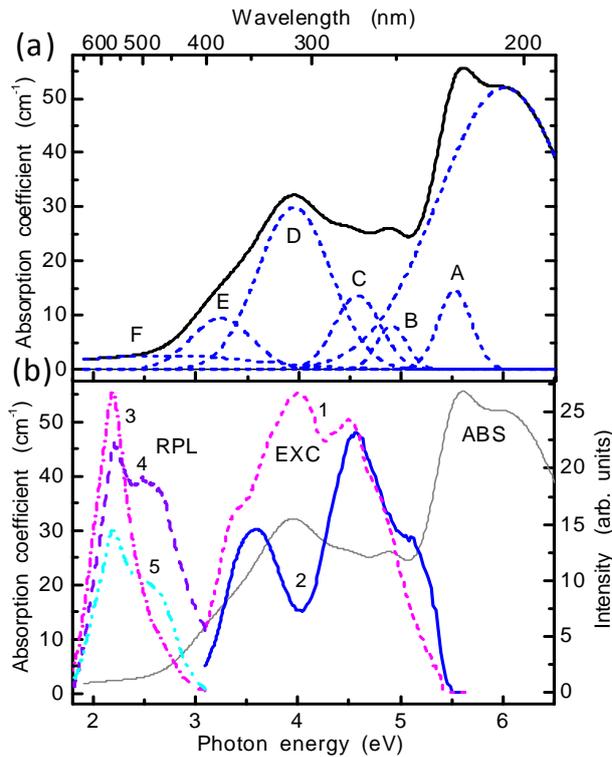

Figure 1. (a) Absorption and (b) excitation and RPL spectra of PG:Ag after X-ray irradiation with a dose of 24.5 Gy. The absorption spectrum was decomposed into the sum of separate Gaussian bands (dashed lines). Excitation was detected at 560 nm (Curve 1) and 450 nm (Curve 2) and RPL was excited at 308 nm (Curve 3), 270 nm (Curve 4) and 345 nm (Curve 5).

Figure 2 shows the absorption spectrum before (Curve 1) and after (Curves 2 and 3) irradiating fs laser pulses in multi-shot mode (1.0×10^5 shots in 1 s) on the non-X-ray-irradiated PG:Ag. Note that Curves 2 and 3 show the difference in absorbance between the 800-nm fs laser-irradiated and non-irradiated regions. The inset shows the excitation and emission spectra corresponding to the absorption spectrum for Curve 2. In the inset an excitation spectrum (solid line) for an emission at 560 nm (orange RPL) and emission spectra for excitations at 308 nm (dashed line) and at 345 nm (dashed-dotted-line) are shown. These spectra of fs irradiation were in good agreement with those of the X-ray irradiation, as shown in Figure 1(b). For Curves 2 and 3, the pulse energy was 2.0 μJ/pulse and 3.0 μJ/pulse at scanning rates of 1000 μm/s and 50 μm/s, respectively. The spot diameter was approximately 2 μm. The light intensity of the laser beam irradiated on the sample was estimated to be 8.0×10^{14} W/cm² for Curve 2 and 1.2×10^{15} W/cm² for Curve 3. For Curve 2, a peak position at 315 nm of the absorption band was in good agreement with that of the X-ray irradiated absorption band, as shown in Figure 1(a).

On the other hand, for Curve 3 the difference in the absorption spectrum was decomposed into a sum of separate Lorentzian bands. As a result, the spectrum was dominated by an absorption band at 404 nm that could be ascribed to the surface plasmon resonance (SPR) of the formed silver nanoparticles [13]. Note that orange or blue emission for an excitation at 404 nm for Curve 3 could not be observed (not shown here). The other broad absorption band from 400 to 600 nm can be attributed to the hole-trap centres corresponding to the "F" band, as shown in Figure 1(a).

The average diameter d of the embedded silver nanoparticles corresponding to Curve 3 was calculated from the decomposed absorption band using the formula $d = V_f\lambda_p^2 / (\pi c\Delta\lambda)$ [14], where V_f is the Fermi velocity of the electrons in bulk silver (~1.39×10^6 m/s), $\Delta\lambda$ is the full-width at half maximum (FWHM) of the absorption band, and λ_p is the characteristic wavelength at which SPR occurs. The average size of the silver nanoparticles was calculated to be approximately 2.8 nm, which is in a good agreement with the observation by TEM [12].
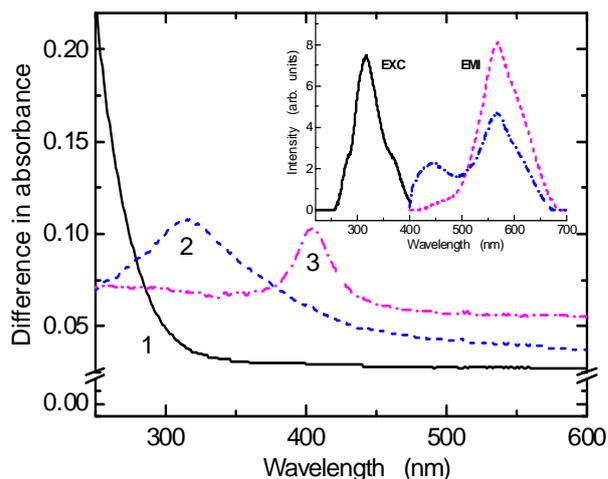

Figure 2. Absorption spectrum before (Curve 1) and after (Curves 2 and 3) irradiating fs laser pulses on the non-X-ray-irradiated PG:Ag. The excitation (solid line) and emission (dashed and dashed-dotted-lines) spectra corresponding to the absorption spectrum for Curve 2 are shown in the inset.

Note that irradiation with X-rays and fs laser pulses yields different absorption peak wavelengths of the Ag^0 centres as described above: the former is 345 nm, and the latter is 404 nm. One of the reasons for this difference is that when fs laser pulses are focused inside the sample at a high repetition rate over 250 kHz, the temperature at the focal point increases to as high as several thousand K [15], a much higher temperature than that reached in normal heat treatment. As a result, highly successive fs laser pulses and a slow scanning rate caused cumulative heating around the focal point. Increasing the temperature greatly increased the average size of nanoparticles formed by fs laser irradiation, resulting in a red-shift of the peak wavelength. Moreover, Ma et al. [11] have reported that the light intensity on the order of 10^{15} W/cm^2 was high enough to generate multi-photon ionisation in the glass matrix, and the heat accumulated by the 250-kHz fs laser resulted in the subsequent Ag nanoparticle growth process.

3.3 Heat treatment

Furthermore, to obtain additional evidence for the band assignments to Ag^0, Ag_2^+, Ag^{2+} and Ag_3^+ centres, heat treatments were performed at temperatures from 295 (room temperature) to 523 K. Before measuring the absorption, excitation and emission spectra of the RPL at each temperature after exposure to X-rays, a 30-min pre-heat was performed at 343 K to suppress the 'build-up' kinetics (i.e., the RPL centre concentration increases as a function of time after irradiation). Finally, the samples were thermally annealed at 673 K for 30 min to eliminate stable colour centres before they were used again.

Figure 3 shows absorption and excitation spectra at annealing temperatures of 295 and 523 K. The band peaking at 345 nm due to the Ag^0 centres shifted from 345 nm (solid line) at 295 K to 330 nm (dashed-and-double-dotted line) at 523 K with increasing annealing temperature. A similar phenomenon also appeared in optical absorption spectra taken on the gamma-irradiated, silver-doped silicate glass, where the absorption peak is blue-shifted from 345 nm (the characteristic wavelength of Ag^0 atoms) at room temperature to 310 nm at 633 K [16]. A blue shift from 270 to 260 nm was also

observed for the 270 nm band with increasing annealing temperatures, as shown in figure 3(a). The blue shift can be explained by the reaction of neutral silver with Ag^+, i.e., $Ag^0 + Ag^+ \rightarrow Ag_2^+$, which therefore shifts the position of the Ag^0 band. The Ag_2^+ band with coupling to Ag^0 atoms also blue-shifts from the original position at room temperature. The complete set of results taken from 295 to 523 K showed that the maximum intensity of the blue excitation bands peaking at 270 and 345 nm occurred at 343 K. These bands then decreased gradually in intensity with increasing temperature. Moreover, another larger band peaking at 244 nm (corresponding to "B") appeared after annealing at 523 K, which may be attributed to the formation of Ag_3^+ ($Ag^0 + Ag_2^+ \rightarrow Ag_3^+$) or Ag_3^{2+} ($Ag^+ + Ag_2^+ \rightarrow Ag_3^{2+}$) from the diffusion and dimerisation of Ag_2^+ ions.

In contrast, the band peaking at 308 nm due to Ag^{2+} without coupling to Ag^0 centres remained in essentially the same peak position as shown in Figure 3(b); the intensity of the excitation band at 308 nm for the orange RPL at 560 nm increased monotonically with increasing temperature.
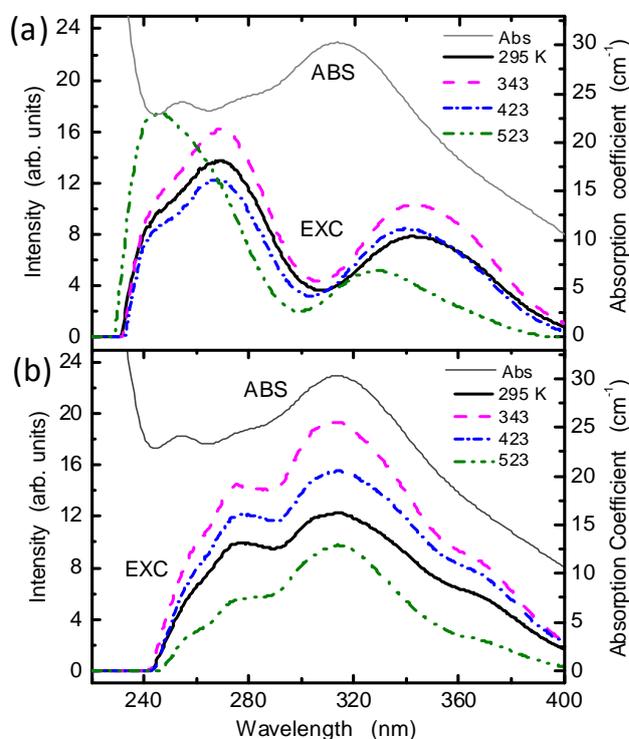

Figure 3. Excitation spectra of the irradiated PG:Ag at different annealing temperatures for detection at (a) 450 nm and (b) 560 nm. Excitation spectra after different annealing temperatures: Excitation detected at 295 K (solid line), 343 K (dashed line), 423 K (dashed-and-dotted line) and 523 K (dashed-and-double-dotted line).

3.4 RPL decay curve analysis
Next, to investigate the change in the blue RPL over time by observing the 270- and 345-nm bands, the lifetime measurements were performed at room temperature. Table 1 summarises the results of the measured lifetimes at 450 nm for different doses, which were obtained by fitting the exponential components with the use of a least-squares iteration deconvolution method to the decay curves. The relative strength of the lifetimes are also given in parentheses in Table 1. The excitation wavelengths for the 270- and 345-nm bands were monochromatised using suitable interference filters. In the case of 345-nm excitation, the lifetime values are almost independent of the absorbed doses ranging from 1.22 to 24.5 Gy and are about 5.6 ns. In contrast, the lifetime values of 270-nm excitation are strongly dependent on the dose, particularly for doses less than 2.45 Gy, where the lifetime values drastically shorten to 2-3 ns. This result supports the other evidence on the different origin and structures of the 270- and 345-nm bands. In the case of lower doses, photoluminescence (PL) at 302 nm excited by the Ag^+ band becomes predominant, and thus a shoulder part of the PL completely overlaps a blue RPL at

450 nm. If the PL is detected instead of emission due to the Ag_2^+ centres, the lifetime value becomes much longer, about 8600 ns, as already reported in [8]. Therefore, one reason for these shorter lifetime values may be the 'perturbation effect' of the excited state $(Ag_2^+)^*$ level by stronger emission of PL. However, more detailed information is needed for a satisfactory explanation.

Table 1. Radiative lifetime values as measured for the blue RPL at 450 nm excited at 270 nm and 345 nm for PG:Ag. X-ray doses from 1.22 to 24.5 Gy.

Doses (Gy)	Lifetime (ns) @270 nm	Lifetime (ns) @345 nm
1.22	3.31 (79.5%)	5.56 (71.7%)
2.45	2.40 (55.7%)	5.44 (76.8%)
7.35	6.32 (63.3%)	5.67 (73.0%)
12.2	6.38 (62.0%)	5.71 (72.6%)
24.5	6.15 (63.8%)	5.63 (75.7%)

3.5 RPL readout system

As previously described, the blue emission at 450 nm and orange emission at 560 nm in PG:Ag were confirmed to be the radiation-induced colour centres. Therefore, it is not necessary to use a time-resolved technique to discriminate the orange RPL from short- and long-term components, which were regarded as parasitic luminescence. We have proposed and constructed a new readout system with a modulated cw UV laser diode as an excitation and phase-sensitive method instead of a time-resolved technique.

Figure 4 presents a schematic view of the experimental setup for the RPL measurement. The excitation source is a 16-mW, cw laser diode (Coherent, CUBE 375-16C) at 371 nm that provides a linearly polarised output beam with $M^2 < 1.2$. The laser diode was modulated by a rectangular waveform at frequencies up to 70 kHz (average power: P_{ave}=2.5 mW, peak power density: P_{peak}< 50 W/cm^2), and a portion of the driving voltage was fed as a reference signal of a lock-in amplifier (NF, LI-574A). The blue and orange RPLs were detected with a photomultiplier (Hamamatsu, R1463) through appropriate filters and then amplified by a lock-in-amplifier.

Figure 5 shows typical orange RPL output in the X-ray irradiated PG:Ag (**a**) with various doses from 82 to 320 mGy and (b) with a dose of 30 mGy. In general, the glass dosimeter GD-450 used in this work is set in a plastic holder with embedded metal and plastic filters used for the discrimination of radiation [6]. In Figure 5(a), X-ray irradiation was determined without the plastic holders, while in Figure 5(b) it was measured with plastic holders partially shielded by metal and plastic filters. The measurements were performed according to the following procedure: first, after X-ray irradiation, the background signal (dashed line) corresponding to the pre-dose fluorescence of the glass surface, stray light and dirt was obtained from the samples in non-irradiated areas. Second, the orange RPL signal was measured by repeatedly scanning irradiated areas of the samples. Finally, the RPL intensities were obtained by subtracting the averaged background signal from the averaged RPL value. Figure 5(a) shows experimental results of the relationship between the RPL intensity and the absorbed doses of the glass dosimeter, demonstrating a linear relationship. Figure 5 (b) shows the measured RPL intensity obtained from the X-ray irradiated PG:Ag with a dose of 30 mGy with plastic holders containing a sample partly shielded by metal and plastic filters. In general, the use of various filters

gives additional information about incident radiation qualities such as gamma-, beta- and X-rays by measuring the RPL intensity ratio [17]. In this case, the ratio of X-rays was similar to that of beta-rays, which may be due to the low energy photons of about 8 keV. Consequently, the new readout system with a modulated cw UV laser diode as an excitation and phase-sensitive method has considerable potential for the measurement of the RPL of glass dosimeters.
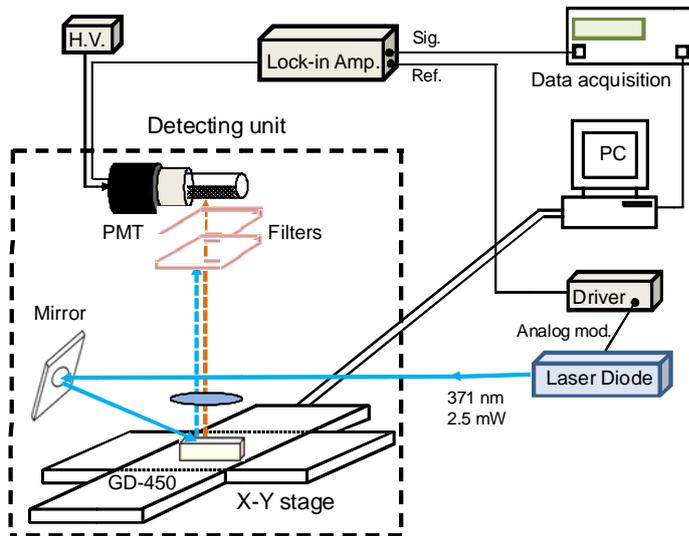

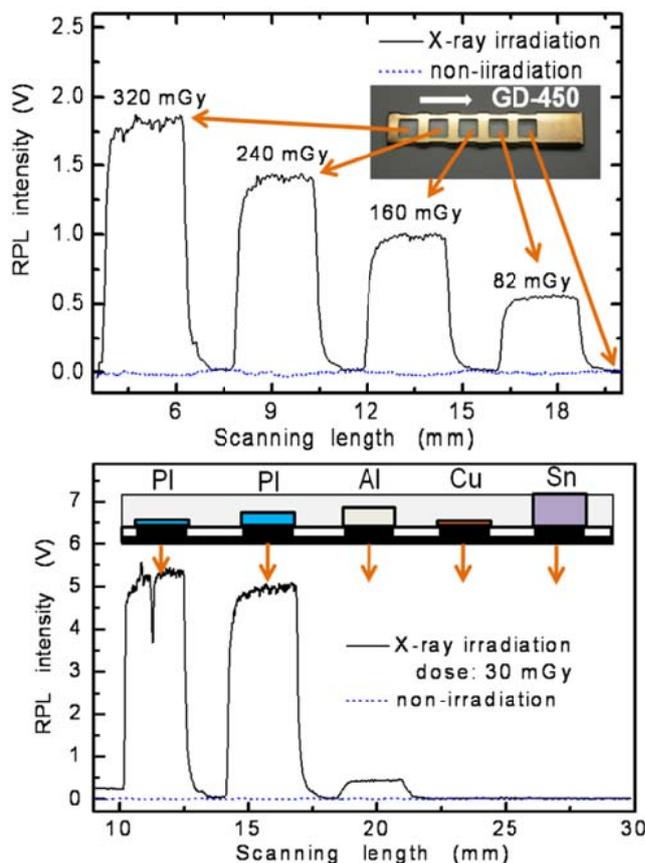**Figure 4.** Schematic setup for the RPL measurement of the glass dosimeter.

Figure 5. Measured RPL intensity as a function of the horizontal scanning length (a) without the plastic holders and (b) with the plastic holders containing metals and plastic filters. The filters and thicknesses (in mm) were: Pl (0.22), Pl (0.5), Al (0.7), Cu (0.2) and Sn (1.2). 'Pl' indicates a plastic filter. The PG:Ag sample was irradiated with X-rays (a) with doses ranging from 82 to 320 mGy and (b) with a dose of 30 mGy.

4. Conclusion

The data obtained in this study allow for the following conclusions:

(1) An absorption band of X-ray irradiated PG:Ag could be decomposed into six Gaussian bands, marked as "A" to "F", peaking at 225, 252, 270, 307, 354 and 424 nm for PG:Ag, respectively.

(2) Through fs laser pulse exposure, heat treatment, and lifetime measurements, the "A" band at 225 nm, the "B" band at 252 nm, the "C" band at 270 nm, the "D" band at 307 nm, the "E" band at 354 nm, and the "F" band at 424 nm were attributed to Ag^+, Ag_3^+ or Ag_3^{2+}, Ag_2^+, Ag^{2+}, Ag^0 and hole-trap centres, respectively.

(3) In the absorbed-dose range of 1.22-24.5 Gy, no components of the blue and orange emissions could be attributed to dirt or any pre-dose. All components of the blue and orange emissions in PG:Ag were confirmed to be radiation-induced colour centres. In particular, the lifetime of the blue RPL excited at 345 nm remained constant for various doses, while that of the blue RPL excited at 270 nm centres were strongly dependent on the absorbed doses.

(4) Preliminary experimental results were demonstrated using a home-made reader based on a modulated UV laser diode and a phase-sensitive technique that we proposed and constructed.

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