

Assignments and optical properties of X-ray-induced colour centres in blue and orange radiophotoluminescent silver-activated glasses

メタデータ	言語: eng 出版者: 公開日: 2017-10-03 キーワード (Ja): キーワード (En): 作成者: メールアドレス: 所属:
URL	http://hdl.handle.net/2297/25783

Author's Accepted Manuscript

Assignments and optical properties of X-ray-induced colour centres in blue and orange radiophotoluminescent silver-activated glasses

Wang Zheng, Toshio Kurobori

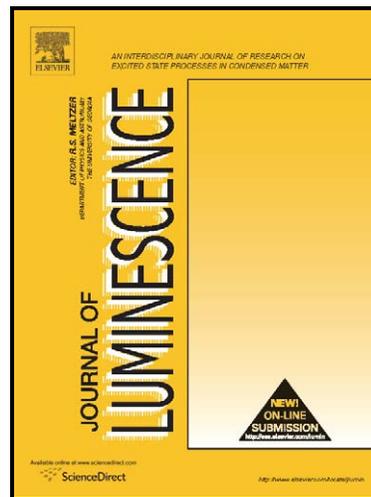
PII: S0022-2313(10)00357-1
DOI: doi:10.1016/j.jlumin.2010.08.024
Reference: LUMIN 10281

To appear in: *Journal of Luminescence*

Received date: 11 May 2010
Revised date: 5 August 2010
Accepted date: 23 August 2010

Cite this article as: Wang Zheng and Toshio Kurobori, Assignments and optical properties of X-ray-induced colour centres in blue and orange radiophotoluminescent silver-activated glasses, *Journal of Luminescence*, doi:10.1016/j.jlumin.2010.08.024

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting galley proof before it is published in its final citable form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



www.elsevier.com/locate/jlumin

Assignments and optical properties of X-ray-induced colour centres in blue and orange radiophotoluminescent silver-activated glasses

Wang Zheng^a and Toshio Kurobori^{a,*}

^a Graduate School of Natural Science and Technology, Kanazawa University, Kakuma-machi, Kanazawa, Ishikawa 920-1192, Japan

ABSTRACT

We have systematically investigated the origin and optical properties of the X-ray-induced colour centres based on the blue and red radiophotoluminescence (RPL) in a silver-activated phosphate glass. The induced-absorption band was decomposed into six Gaussian bands on the basis of its strong analogy with silver-activated sodium chloride. We have ascribed these bands to Ag^0 , Ag^{2+} , Ag_2^+ and other silver ion species by means of optical and thermal measurements such as colour centre formation and dissolution by highly successive femtosecond-pulse irradiation, excited-state lifetime and thermal annealing characteristics. The data confirmed that the blue RPL at 450 nm could be attributed to the 270 and 345 nm bands due to the Ag_2^+ and Ag^0 centres, respectively, and that the orange RPL at 560 nm was associated with the 308 nm band due to the Ag^{2+} centres.

PACS: 78.55.Hx, 81.05.Kf

Keywords: Radiophotoluminescence, Silver-doped phosphate glass, Glass dosimeter, Sodium chloride, Femtosecond laser pulse

*Corresponding author. fax: +81-76- 234-4132

*E-mail address: laser@kenroku.kanazawa-u.ac.jp (T. Kurobori)

1. Introduction

Radiophotoluminescence (RPL) in various glasses containing silver impurities has long been examined [1-4] for applications in personal solid-state dosimetry and radiation measurements. In particular, radiation-induced colour centres have been extensively studied in silver-activated glasses by means of optical spectroscopy [1, 4] and the electron spin resonance (ESR) method [2-4]. Later, the nucleation and growth kinetics of silver nanoparticles in glass were investigated in detail [5]. Furthermore, the influence of glass composition on the sensitivity to ionising radiation and the RPL ‘build-up’ kinetics (i.e., the RPL centre concentration increases as a function of time after irradiation) have been also studied [6]. At the same time, a readout system for the detection of RPL from a glass dosimeter has been developed using a pulsed ultraviolet (UV) nitrogen laser [7] and a UV light emitting diode (LED) [8] as an excitation source. Although the study of the RPL ‘build-up’ kinetics and development of the readout system address the most important problems for practical applications of radiophotoluminescent glass dosimeters, successful work has not yet been achieved.

In addition, recent advances in high-intensity femtosecond (fs) laser pulses have made it possible to fabricate small noble metal particles [9-11] such as gold and silver atoms embedded in glasses as well as encode various functional microstructures inside transparent materials [12-14]. In particular, such metal nanoparticles embedded in glasses are expected to

1 be promising materials for functional optical devices due to a large third-order nonlinear
2
3
4 susceptibility and an ultrafast nonlinear response [15]. As far as silver-doped phosphate glass,
5
6
7 Y. Watanabe et al. [10] demonstrated a photosensitivity in soda-alumina-phosphate glass
8
9
10 doped with Ag^+ upon exposure to UV fs laser pulses and found the formation of colour
11
12
13 centres such as Ag^0 and Ag^{2+} in the glass. Q. Zhao et al. [11] investigated the precipitation
14
15
16 and dissolution of nanoparticles in Ag^+ -doped phosphate glass by irradiation with a
17
18
19 near-infrared (IR) 800 nm fs laser pulses and further annealing at various temperatures. The
20
21
22 process of the formation of Ag^+ -related colour centres in the glass, especially Ag^0 and Ag^{2+} ,
23
24
25 can be explained as a consequence capturing photo-excited electron or hole onto Ag^+ via
26
27
28 multi-photon absorption induced by extremely high-peak power densities of fs laser pulses.
29
30
31 Subsequent heat treatment leads to the formation of Ag^0 centres and the dissolution of Ag^{2+}
32
33
34 centres.
35
36

37
38 This paper systematically examines the assignments and optical properties of
39
40
41 X-ray-induced colour centres such as Ag^0 , Ag_2^+ , Ag^{2+} and other silver ion species, as the
42
43
44 spectral contribution of these small clusters to the overall spectrum of silver-activated
45
46
47 phosphate glass (PG:Ag) is not known at present. To determine the induced colour centres in
48
49
50 PG:Ag and obtain additional evidence of their assignments, measurements such as absorption,
51
52
53 excitation, emission, colour centre formation by fs laser pulse irradiation, radiative lifetime
54
55
56 and thermal treatment were carried out. In particular, direct precipitation of silver
57
58
59
60
61
62
63
64
65

1 nanoparticles in Ag⁺-activated phosphate glass without heat treatment was demonstrated for
2
3
4 the first time to clarify the origin of a RPL glass dosimeter by highly successive fs laser
5
6
7 pulses. Moreover, silver-activated sodium chloride (NaCl:Ag) as an additional sample was
8
9
10 also used for comparison.
11

12 13 14 15 16 17 **2. Experimental details** 18

19
20
21
22
23 A commercially available GD-450 dosimeter (AGC Techno Glass Co. Ltd.) was used as
24
25
26 the radiophotoluminescent PG:Ag. Samples were cut from the original glass dosimeter plate
27
28
29 to a size of approximately $10 \times 7 \times 1 \text{ mm}^3$. The weight composition of the GD-450 dosimeter
30
31
32 was 31.55% P, 51.16% O, 6.12% Al, 11.00% Na and 0.17% Ag. Additional samples without
33
34
35 Ag (PG-glass and NaCl-crystalline matrix) were used as reference samples.
36

37
38
39 All samples were coloured by irradiation from an X-ray unit (dose rate: 12 mGy/min)
40
41
42 with a copper target operated at 30 kV and 20 mA. In this work, the samples were irradiated
43
44
45 such that the absorbed doses ranged from 1.22 to 24.5 Gy. Absorption, excitation and
46
47
48 emission measurements were performed at room temperature using a Hitachi U-2010 UV-VIS
49
50
51 and an F-2500 fluorescence spectrophotometer. Radiative lifetime measurements were
52
53
54 performed using a time-resolved spectrofluorometer (Horiba Ltd., NAES-1100), which was
55
56
57 operated based on the time-correlated multi-photon counting technique [16]. A high-pressure
58
59
60
61
62
63
64
65

1 lamp emitted light pulses with stable intensities, a full-width at half maximum (FWHM) of
2
3
4 less than 2 ns and a repetition rate of 7 kHz. The excitation wavelength was monochromatised
5
6
7 using interference filters with a central wavelength of 340 nm. The RPL from the crystal was
8
9
10 observed in a direction perpendicular to that of the excitation beam and analysed using
11
12
13 suitable filters with central wavelengths of 450 nm (blue RPL) and 560 nm (orange RPL),
14
15
16 respectively.
17

18
19
20 For the direct photo-induced reduction from Ag^+ ions to Ag^0 centres in PG:Ag, this work
21
22
23 used a regeneratively amplified 800 nm Ti:sapphire laser that emits 120 fs, 250 kHz
24
25
26 mode-locked pulses. The fs laser pulses were focused using a 20× objective lens with a
27
28
29 numerical aperture (NA) of 0.40 to a depth of 250 μm beneath the sample surface with the
30
31
32 help of a computer-controlled 3D X-Y-Z stage with a rate of 50 $\mu\text{m}/\text{s}$ and a pitch of 20 μm .
33
34
35 The pulse energy was 3.0 $\mu\text{J}/\text{pulse}$ and the spot diameter was approximately 2 μm . The
36
37
38 numbers of successive pulses at the focal points were 1.0×10^5 shots in 1 s. A square $5 \times 5 \text{ mm}^2$
39
40
41 area was written inside the sample line by line using the intense and high repetition rate fs
42
43
44 laser pulses to measure the absorption spectra of the irradiation region inside the glass sample.
45
46
47
48
49
50

51 **3. Results and discussion**

52
53
54
55
56
57
58
59
60
61
62
63
64
65

1 Fig. 1 shows the absorption (solid line) and excitation spectra (dashed-and-dotted line) of
2
3
4 the irradiated (a) NaCl:Ag and (b) PG:Ag under an absorbed dose of 24.5 Gy. All samples
5
6
7 were transparent and colourless before X-ray irradiation, with an absorption edge at about 250
8
9
10 nm for NaCl samples and 300 nm for PG samples. After X-ray irradiation, various
11
12
13 Ag⁺-related colour centres were produced inside the samples of 0.81-mm-thick NaCl:Ag and
14
15
16 1.0-mm-thick PG:Ag, respectively. The absorption coefficient was calculated using the
17
18
19 absorbance of the induced Ag⁺-related band maximum at 275 nm for NaCl:Ag and 315 nm for
20
21
22 PG:Ag, respectively. The glass changed from colourless to slightly yellow after X-ray
23
24
25 irradiation; however this colour formed would not disappear unless heat annealing at 673 K
26
27
28 for 30 min is carried out to use repeatedly. Furthermore, the RPL spectra after X-ray
29
30
31 irradiation for NaCl:Ag and PG:Ag are shown in Figs. 1c and d, respectively. For the
32
33
34 NaCl:Ag and PG:Ag samples, the excitation is in the range of 250-400 nm (left-hand side)
35
36
37 and the emission is in the form of a broad band extending from 400-700 nm (right-hand side).
38
39
40 In addition, both absorption spectra were decomposed into the sum of separate Gaussian
41
42
43 bands (indicated by a dashed line).
44
45
46
47

48 In the case of NaCl:Ag, the absorption band in Fig. 1a could be decomposed into six
49
50
51 bands, with peaks at 224, 276, 308, 335, 382 and 443 nm. When the silver-activated
52
53
54 alkali-halides were irradiated with X-rays, several new bands appeared next to the
55
56
57 well-known “F”-band (i.e., an electron trapped in an anion vacancy) with a peak at 465 nm in
58
59
60
61
62
63
64
65

1 pure NaCl. These new bands are respectively designated as the “A”, “B”, “C”, “D” and “E”
2
3
4 bands, as described in Ref. [17]. Parfianovich et al. [18] observed induced bands at “B”
5
6
7 (peaking at 278 nm), “C” (310 nm), “D” (335 nm) and “E” (400 nm) in X-ray irradiated
8
9
10 NaCl:Ag. The peak position of each band is in good agreement with the decomposed results
11
12
13 above. Bands peaking at 232 nm (corresponding to “A”) and peaking at 465 nm
14
15
16 (corresponding to “F”) measured in NaCl:Ag are due to $\text{Ag}^+\text{-Ag}^+$ paired ions and F centres,
17
18
19 respectively. In addition, the peak positions of bands “E” and “F” almost overlap the F band,
20
21
22 peaking at 465 nm. Thus, the absorption peaks for the RPL are mainly attributed to bands “B”,
23
24
25
26 “C” and “D”. The origin of these bands in NaCl:Ag has already been clarified [19] as follows:
27
28
29 bands “B” and “D” are related to F and F_2 centres (i.e., two electrons bound to two
30
31
32 neighbouring anion vacancies) with neighbouring Ag^+ , respectively, and the narrow “C” band
33
34
35 is strongly related to the Ag^0 centres.
36
37

38
39 For NaCl:Ag, the excitation spectrum for an emission wavelength at 560 nm (orange
40
41
42 RPL) consists of two explicit peaks at 289 and 339 nm. These peaks are strongly overlapped
43
44
45 by bands “B”, “C” for the former and “D” for the latter, respectively, in the corresponding
46
47
48 absorption spectrum. The other peak at 232 nm is overlapped by band “A”. Bands “E” and
49
50
51 “F” do not contribute to the RPL in the visible region. In addition, the excitation spectrum for
52
53
54 an emission at 450 nm (blue RPL, data not shown) is mainly related to the 232 nm absorption
55
56
57
58
59
60
61
62
63
64
65

1 band and to the 281 nm band. The former is due to the Ag^+-Ag^+ paired ions, and the latter is
2
3
4 due to F centres with minor contributions from neighbouring Ag^+ .
5
6

7 In the case of PG:Ag, the appropriate absorption bands in Fig. 1b could also be
8
9 decomposed into six absorption bands from “A” to “F”, peaking at 225, 252, 270, 307, 354
10
11 and 424 nm [20], respectively. Although the absorption spectra can be decomposed into six
12
13 Gaussian bands, the excitation spectra for both samples are not as complicated as the
14
15 absorption spectra. The excitation spectra consist of two different spectra. One spectrum
16
17 peaks at 308 nm for an emission at 560 nm (orange), and the other peaks at 270 and 345 nm
18
19 for an emission at 450 nm (blue). The former corresponds to the decomposed 307 nm
20
21 Gaussian band, while the latter corresponds to the decomposed 270 and 354 nm bands,
22
23 respectively.
24
25
26
27
28
29
30
31
32
33
34
35

36 For PG:Ag, the blue emission and some portion of the orange emission are strongly
37
38 related to the 270 and 345 nm excitation bands, which is completely analogous to the blue
39
40 emission of NaCl:Ag associated with bands “B” (i.e., the F centres with neighbouring Ag^+)
41
42 and “C” (i.e., the Ag^0 centres). Therefore, based on the above results, the absorption band
43
44 centred at 345 nm in the irradiated PG:Ag may be attributed to Ag^0 centres (reaction: $\text{Ag}^+ + e^-$
45
46 $\rightarrow \text{Ag}^0$). The other blue band at 270 nm in PG:Ag may also be related to the Ag_2^+
47
48 (reaction: $\text{Ag}^0 + \text{Ag}^+ \rightarrow \text{Ag}_2^+$). These attributions are further supported by the following fs
49
50 laser, heat treatment and lifetime measurement experiments. In contrast, the orange emission
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1 in PG:Ag is closely related to the absorption band at 308 nm, which may be attributed to Ag^{2+}
2
3
4 (reaction: $\text{Ag}^+ + h^+ \rightarrow \text{Ag}^{2+}$) centres. This attribution is further supported by the following heat
5
6
7 treatment.

8
9
10 Note that the absorption coefficient of PG:Ag with a maximum at 315 nm was about
11
12 three times larger than that of NaCl:Ag with a maximum at 275 nm under a dose of 24.5 Gy.
13
14 However, as shown in Figs. 1c and d, the orange RPL intensity of PG:Ag with maximum at
15
16 560 nm was nearly two-thirds lower than that of NaCl:Ag under the same dose.
17
18
19
20
21

22
23 Additional evidence to attribute the 345 nm band in X-ray irradiated PG:Ag to Ag^0
24
25 centres was demonstrated by the fs laser experiment. Recently, intense fs laser pulses with
26
27 high-peak power densities ($\sim 100 \text{ TW/cm}^2$) and high repetition rates ($> 200 \text{ kHz}$) have enabled
28
29 direct precipitation of silver nanoparticles in silver-activated silicate glass without heat
30
31 treatment [21]. In the case of silver-activated glasses, it is well known that irradiation with fs
32
33 laser pulses as well as X-rays and subsequent annealing at high temperature ($\sim 770 \text{ K}$) for 10
34
35 min bring about the reduction of Ag^+ ions to Ag^0 atoms and result in the formation of
36
37 plasmonic nanoparticles, as observed by means of luminescence and ESR spectroscopy and
38
39 transmission electron microscopy (TEM). Measurements taken with such intense fs laser
40
41 pulses have played a significant role in the evaluation of RPL characteristics in glasses and in
42
43 the determination of the formation kinetics of related colour centres [10-12].
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1 Fig. 2 shows the absorption spectra of X-ray (Curve 1) and fs laser pulse (Curve 2)
2
3 coloured PG:Ag, respectively. In the case of Curve 1, the absorption spectrum was taken
4
5 under an absorbed dose of 24.5 Gy and the decomposed absorption bands, as shown in Fig.1b,
6
7 at 345 nm (corresponding to “E”) and the broad “F” bands were also shown for comparison.
8
9
10 On the other hand, for Curve 2 the light intensity of the laser beam irradiated on the sample
11
12 was estimated to be 1.2×10^{15} W/cm². A peak position at 345 nm (“E”) of the X-ray irradiated
13
14 absorption band was quite different with that of the fs laser pulse irradiation. Moreover, the
15
16 absorption spectrum of Curve 2 was decomposed into a sum of separate Lorentzian bands, as
17
18 shown in the inset. As a result, the spectrum was dominated by an absorption band at 404 nm,
19
20 which could be ascribed to the surface plasmon resonance (SPR) of the formed silver
21
22 nanoparticles.
23
24
25
26
27
28
29
30
31
32
33

34
35 According to [12], absorption bands peaking at 460 and 620 nm in the Ag⁺-doped silicate
36
37 glass that appeared after the fs laser irradiation were assigned to the hole-trap centres (HC) at
38
39 the nonbridging oxygen in the SiO₄ polyhedron with two and three nonbridging oxygen atoms,
40
41 e.g., HC₁ and HC₂, respectively. After annealing at 773 K for 10 min, the laser-irradiated area
42
43 became light yellow and a peak at 408 nm due to the surface plasmon absorption of the silver
44
45 nanoparticles was observed. In the case of our highly successive fs laser pulses over 250 kHz,
46
47
48
49
50
51 silver nanoparticles inside PG:Ag were precipitated directly without heat treatment. Therefore,
52
53
54
55
56
57 there were no distinct absorption bands peaking at 460 and 620 nm due to the hole-trap
58
59
60
61
62
63
64
65

1 centres. However, the broad absorption band in low intensity from 400 to 600 nm as also
2
3
4 shown could be attributed to the above hole-trap centres, which corresponds to the
5
6
7 decomposed “F” band as shown in Fig. 1b.
8
9

10 The average diameter D of the embedded silver nanoparticles was calculated from the
11
12 decomposed absorption band using the formula $D=V_f\lambda_p^2/(\pi c\Delta\lambda)$ [22], where V_f is the Fermi
13
14 velocity of the electrons in bulk silver ($\sim 1.39\times 10^6$ m/s), $\Delta\lambda$ is the FWHM of the absorption
15
16 band, and λ_p is the characteristic wavelength at which SPR occurs. The average size of the
17
18 silver nanoparticles was calculated to be approximately 2.8 nm, which is in a good agreement
19
20 with the observation by TEM [12].
21
22
23
24
25
26
27
28

29 Note that irradiation with X-rays and fs laser pulses yields different absorption peak
30
31 wavelengths of the Ag^0 centres as described above: the former is 345 nm, and the latter is 404
32
33 nm. One of the reasons for this difference is that when fs laser pulses are focused inside the
34
35 sample at a high repetition rate over 250 kHz, the temperature at the focal point increases to
36
37 as high as several thousand K [23], a much higher temperature than that reached in normal
38
39 heat treatment. As a result, highly successive fs laser pulses cause the accumulation of heat
40
41 around the focal point. Increasing the temperature greatly increased the average size of
42
43 nanoparticles formed by fs laser irradiation, resulting in a red-shift of the peak wavelength. In
44
45 addition to this effect, Podlipensky et al. pointed out [24] that the SP resonance depends
46
47 strongly on the size, shape, distribution and concentration of the nanoparticles. Multi-shot
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1 irradiation with p-polarisation causes preferential orientation along the axis of laser
2
3 polarisation. As a result, the shape of the silver nanoparticles changes from spherical to
4
5
6 oblong, resulting in a red-shift.
7
8
9

10 Furthermore, to obtain additional evidence for assigning each band to Ag^0 , Ag_2^+ and Ag^{2+}
11
12 centres, heat treatments were performed at various temperatures of 295, 343, 423 and 523 K,
13
14 respectively. The samples were kept for one day in the dark after X-ray irradiation and then
15
16 annealed at each temperature for 30 min. After holding the samples at room temperature in
17
18 the dark for another day to suppress the ‘build up’ effect, the absorption, excitation and
19
20 emission of the RPL spectra were measured at 295 K. Finally, the samples were thermally
21
22 annealed at 673 K for 30 min to eliminate stable colour centres before they were used again.
23
24 Selected from this body of data, Fig. 3 shows excitation spectra at annealing temperatures of
25
26 295 and 523 K. The band peaking at 345 nm (corresponding to “E” band) due to the Ag^0
27
28 centres shifted from 345 nm (Fig. 3a) at 295 K to 330 nm (Fig. 3b) at 523 K with increasing
29
30 annealing temperature. A similar phenomenon also appeared in optical absorption spectra
31
32 taken on the gamma irradiated silver-doped silicate glass, where the absorption peak is
33
34 blueshifted from 345 nm (the characteristic wavelength of Ag^0 atoms) at room temperature to
35
36 310 nm at 633 K [25]. This phenomenon represents that annealing the sample at higher
37
38 temperature leads to the disappearance of the Ag^0 centres by the following reaction, i.e., Ag^0
39
40 $\rightarrow \text{Ag}^+ + e^-$. A blue shift from 270 to 260 nm was also observed for the 270 nm
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1 (corresponding to “C”) band with increasing annealing temperatures. This blue shift can be
2
3
4 explained by the reaction of neutral silver with Ag^+ , i.e., $\text{Ag}_2^+ \rightarrow \text{Ag}^0 + \text{Ag}^+$, which therefore
5
6
7 shifts the position of the Ag^0 band. The Ag_2^+ band with coupling to Ag^0 atoms also blueshifts
8
9
10 from the original position at room temperature. The complete set of results taken at 295, 343,
11
12
13 423 and 523 K showed that the maximum intensity of the blue excitation bands peaking at
14
15
16 270 and 345 nm occurred at 343 K. These bands then decreased gradually in intensity with
17
18
19 increasing temperature. Moreover, another larger band peaking at 244 nm (corresponding to
20
21
22 “B”) band appeared after annealing at 523 K, which may be attributed to the formation of
23
24
25 Ag_3^{2+} ($\text{Ag}^+ + \text{Ag}_2^+ \rightarrow \text{Ag}_3^{2+}$) or Ag_3^+ ($\text{Ag}^0 + \text{Ag}_2^+ \rightarrow \text{Ag}_3^+$) from the diffusion and dimerisation
26
27
28 of Ag_2^+ ions.
29
30

31
32 In contrast, the band peaking at 308 nm due to Ag^{2+} without coupling to Ag^0 centres
33
34
35 remained in essentially the same peak position [20]; the intensity of the excitation band at 308
36
37
38 nm for the orange RPL at 560 nm increased monotonically with increasing temperature.
39
40

41
42 Next, to investigate the change in the blue RPL over time by observing the 270 and 345
43
44
45 nm bands, the lifetime measurements were performed at room temperature. The sample was
46
47
48 irradiated with various doses ranging from 1.22 to 24.5 Gy to examine the dose dependence
49
50
51 of the blue RPL radiative lifetime. Table 1 summarises the results of the measured lifetimes at
52
53
54 450 nm for different doses, which were obtained by fitting the exponential components with
55
56
57 the use of a least-squares iteration deconvolution method to the decay curves. The excitation
58
59
60
61
62
63
64
65

1 wavelengths for the 270 and 345 nm bands were monochromatised using suitable interference
2
3
4 filters. In the case of 345 nm excitation, the lifetime values are almost independent of the
5
6
7 absorbed doses ranging from 1.22 to 24.5 Gy and are about 5.6 ns. In contrast, the lifetime
8
9
10 values of 270 nm excitation are strongly dependent on the dose, in particular for lower doses
11
12
13 less than 2.45 Gy, where the lifetime values drastically shorten to 2-3 ns. This result supports
14
15
16 the other evidence on the different origin and structures for the 270 and 345 nm bands. In the
17
18
19 case of lower doses, photoluminescence (PL) at 302 nm excited by the Ag^+ band becomes
20
21
22 predominant, and thus a shoulder part of the PL completely overlaps a blue RPL at 450 nm.
23
24
25 Fig. 4 shows the RPL spectra in PG:Ag excited at 270, 310 and 345 nm, respectively, after
26
27
28 X-ray irradiation under an absorbed dose of 1.22 Gy. If the PL is detected instead of emission
29
30
31 due to the Ag_2^+ centres, the lifetime value becomes much longer about 8600 ns, as already
32
33
34 reported in [20]. Therefore, one of the reasons for these shorter lifetime values may be
35
36
37 attributed to the ‘perturbation effect’ of the excited state $(\text{Ag}_2^+)^*$ level by stronger emission of
38
39
40 PL. However, more detailed information is needed for a satisfactory explanation.
41
42
43
44

45 In contrast, for higher absorbed doses up to 24.5 Gy (not shown here), the blue and
46
47
48 orange RPL intensities drastically decreased due to their concentration quenching, and the
49
50
51 lifetime values also decreased for both the 270 and 345 nm excitations.
52
53
54
55
56
57

58 **4. Conclusions**

59
60
61
62
63
64
65

1
2 We performed optical and thermal measurements on radiophotoluminescent
3
4
5 silver-activated phosphate glass to clarify the origin and characteristics of the X-ray-induced
6
7
8 colour centres. The data obtained enabled the following conclusions:
9

10
11 (1) The RPL absorption study of X-ray irradiated silver-activated phosphate glass (PG:Ag) in
12
13 correlation to NaCl:Ag established that the absorption coefficient of PG:Ag was about three
14
15 times larger than that of NaCl:Ag. On the contrary, the orange RPL intensity of PG:Ag was
16
17 nearly two-thirds lower than that of NaCl:Ag under the same dose.
18
19
20
21

22
23 (2) Both absorption bands of X-ray irradiated PG:Ag and NaCl:Ag could be decomposed into
24
25 six Gaussian bands, marked as “A” to “F”, peaking at 224, 276, 308, 335, 382 and 443 nm for
26
27 NaCl:Ag and at 225, 252, 270, 307, 354 and 424 nm for PG:Ag, respectively.
28
29
30
31

32
33 (3) Blue RPL at 450 nm was closely connected to the 270 and 345 nm bands of the excitation
34
35 spectrum. These bands were attributed to the Ag_2^+ and Ag^0 centres, respectively, through
36
37 highly successive fs laser pulse irradiation, heat treatment and lifetime measurements. The
38
39 Ag^0 centres were sensitive to annealing temperature, and the band peak shifted to shorter
40
41 wavelength with increasing temperature. On the other hand, orange RPL at 560 nm was
42
43 associated with the 308 nm band in the excitation spectrum. This optical activity was due to
44
45 the Ag^{2+} centres, and no blue shift was observed for the Ag^{2+} centres with increasing
46
47 temperature.
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1 (4) The light intensity on the order of 10^{15} W/cm² was high enough to generate multi-photon
2
3
4 ionisation in the Ag-activated phosphate glass matrix and the heat accumulated by the
5
6
7 250-kHz fs laser resulted in direct formation of surface plasmonic Ag nanoparticles.
8

9
10 (5) In the absorbed-dose range of 1.22-24.5 Gy, no components of the blue and orange
11
12
13 emissions were attributable to dirt or any predose. All components of the blue and orange
14
15
16 emissions in PG:Ag were confirmed to be radiation-induced colour centres. The lifetime of
17
18
19 the blue RPL at 450 nm is much shorter than that of the orange RPL at 560 nm (~2170 ns
20
21
22 [20]). In particular, the lifetime of the blue RPL excited at 345 nm remained constant for
23
24
25 various doses, while that of the blue RPL excited at 270 nm centres were strongly dependent
26
27
28 on the absorbed doses.
29
30
31

32 33 34 35 **Acknowledgements**

36
37
38
39 We would like to thank Ms. Y. Miyamoto and Dr. T. Yamamoto at Chiyoda Technol
40
41
42 Corporation for their contributions to the sample preparation and Prof. H. Nanto at Kanazawa
43
44
45 Institute of Technology for his valuable discussions. We would also like to thank Dr. M.
46
47
48 Sakakura, Dr. Y. Shimotsuma, Prof. K. Miura and Prof. K. Hirao at Kyoto University for their
49
50
51 contributions to the femtosecond laser experiments.
52
53
54
55
56
57
58
59
60
61
62
63
64
65

Figure captions

1
2
3
4 **Fig. 1.** Absorption and excitation spectra of (a) NaCl:Ag and (b) PG:Ag after X-ray
5 irradiation with a dose of 24.5 Gy. Both absorption spectra were
6 decomposed into the sum of separate Gaussian bands (dashed lines).
7 Numbers on the right of both excitation spectra indicate the scaling factor as
8 shown in Fig. 1b. RPL emission spectra after X-ray irradiation for (c)
9 NaCl:Ag and (d) PG: Ag. For NaCl:Ag, RPL was excited at 289 nm (solid
10 line) and 339 nm (dashed line). For PG:Ag, RPL was excited at 308 nm
11 (solid line), 270 nm (dashed line) and 340 nm (dashed-and-dotted line).
12
13
14
15
16
17
18
19

20
21 **Fig. 2.** Typical absorption spectra of the silver-activated phosphate glass after X-ray
22 (Curve 1) irradiation under an absorbed dose of 24.5 Gy and after fs laser
23 pulse (Curve 2) irradiation with a peak power density of 1.2×10^{15} W/cm².
24 For Curve 1, the absorption spectrum was decomposed into “E” and “F”
25 bands for comparison. Curve 2 was decomposed into a sum of separate
26 Lorentzian bands as shown in the inset.
27
28
29
30

31
32 **Fig. 3.** Excitation spectra of X-ray irradiated silver-activated phosphate glass at
33 different annealing temperatures at 295 K (a) and 523 K (b) for detection at
34 450 nm. Each spectrum was decomposed into Gaussian bands and marked
35 as the “B”, “C” and “E” bands, respectively.
36
37
38

39
40 **Fig. 4.** RPL spectra in the silver-activated phosphate glass excited at 270, 310 and
41 345 nm after X-ray irradiation with an absorbed dose of 1.22 Gy.
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

Table captions

Table 1 Radiative lifetime values as measured for the blue RPL at 450 nm excited at 270 and 345 nm in the silver-activated phosphate glass with different X-ray doses from 1.22 to 24.5 Gy.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

Accepted manuscript

References

- 1
2 [1] J. H. Schulman, R. J. Ginther, C. C. Klick, R. S. Alger, R. A. Levy, J. Appl. Phys. 22
3 (1951) 1479.
4
5 [2] R. Yokota, S. Nakajima, Health Phys. 11 (1965) 241.
6
7 [3] R. Yokota, H. Imagawa, J. Phys. Soc. Japan 23 (1966) 1038.
8
9 [4] T. Feldmann, A. Treinin, J. Chem. Phys. 47 (1967) 2754.
10
11 [5] U. Kreibig, Appl. Phys. 10 (1976) 255 .
12
13 [6] A. V. Dmitryuk, S. E. Paramzina, A. S. Perminov, N. D. Solov'eva, N. T. Timofeev,
14 J. Non-Cryst. Solids 202 (1996) 173.
15
16 [7] E. Piesch, B. Burgkhardt, M. Fischer, H. G. Röber, S. Ugi, Rad. Prot. Dos. 17 (1986)
17 293.
18
19 [8] Y. Ihara, A. Kishi, W. Kada, F. Sato, Y. Kato, T. Yamamoto, T. Iida, Rad. Meas. 43
20 (2008) 542.
21
22 [9] I. Tanahashi, M. Yoshida, Y. Manabe, T. Tohda, J. Mater. Res. 16 (1995) 362.
23
24 [10] Y. Watanabe, G. Namikawa, T. Onuki, K. Nishio, T. Tsuchiya, Appl. Phys. Lett. 78
25 (2001) 2125.
26
27 [11] Q. Zhao, J. Qiu, X. Jiang, C. Zhao, C. Zhu, Opt. Express 12 (2004) 4035.
28
29 [12] Y. Shimotsuma, K. Hirao, P. G. Kazansky, J. Qiu, Jpn. J. Appl. Phys. 44 (2005) 4735.
30
31 [13] K. Kawamura, M. Hirano, T. Kurobori, D. Takamizu, T. Kamiya , H. Hosono, Appl.
32 Phys. Lett. 84 (2004) 311.
33
34 [14] T. Kurobori, T. Sakai , S. Aoshima, Phys. Status Solidi A 204 (2007) 699.
35
36 [15] Y. Takeda, O. A. Plaksin, N. Kishimoto, Opt. Express 15 (2007) 6010.
37
38 [16] T. Kurobori, T. Kanasaki, Y. Imai, N. Takeuchi, J. Phys. C Solid State Phys. 21 (1988)
39 L397.
40
41 [17] J. H. Schulman , W. D. Compton, *Color Centers in Solids* (Pergamon Press, Inc., New
42 York, 1963) p.160.
43
44 [18] I. A. Parfianovich, E. E. Penzina, Yu. G. Penzin, V.U.Z., Izvestiya, Fizika 2 (1965) 150.
45
46 [19] E. Burstein, J. J. Oberly, B. Hennis, M. White, Phys. Rev. 86 (1955) 255.
47
48 [20] T. Kurobori, W. Zheng, Y. Miyamoto, H. Nanto, T. Yamamoto, Opt. Mater. 32 (2010)
49 1231.
50
51 [21] N. H. Ma, H. L. Ma, M. J. Zhong, J. Y. Yang, Y. Dai, G. Ye, Z. Y. Yue, G. H. Ma , J. R.
52 Qiu, Mater. Lett. 63 (2009) 151.
53
54 [22] G. Mie, Ann. Phys. 25 (1908) 377.
55
56 [23] M. Sakakura, M. Shimizu, Y. Shimotsuma, K. Miura, K. Hirao, Appl. Phys. Lett. 93
57 (2008) 231112.
58
59 [24] A. V. Podlipensky, V. Grebenev, G. Seifert, H. Graener, J. Lumin. 109 (2004) 135.
60
61
62
63
64
65

[25] R. Espiau de Lamaestre, H. Béa, H. Bernas, J. Belloni, J. L. Marignier, Phys. Rev. B 76
(2007) 205431.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

Accepted manuscript

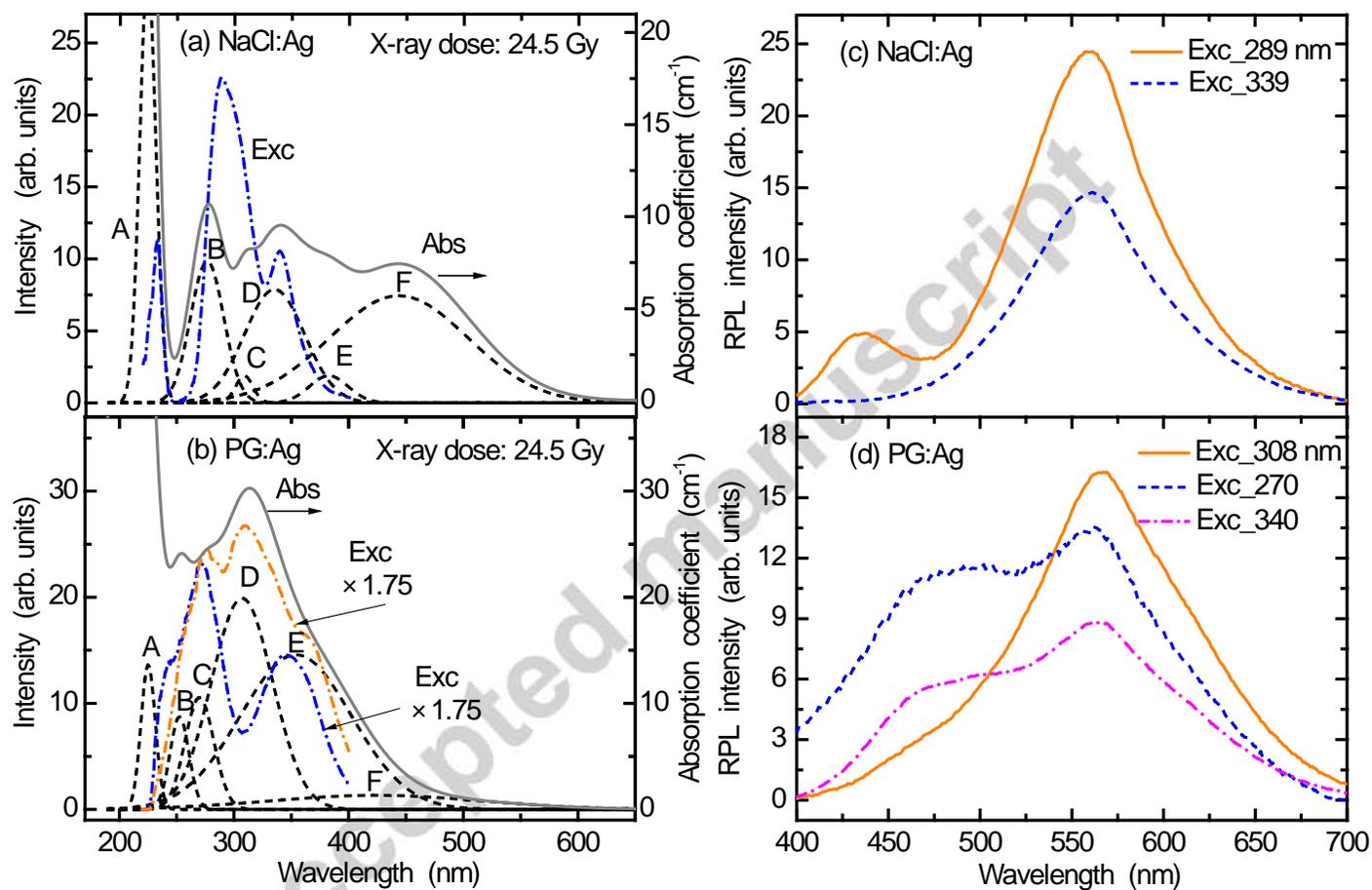
Table

W. Zheng

Table 1

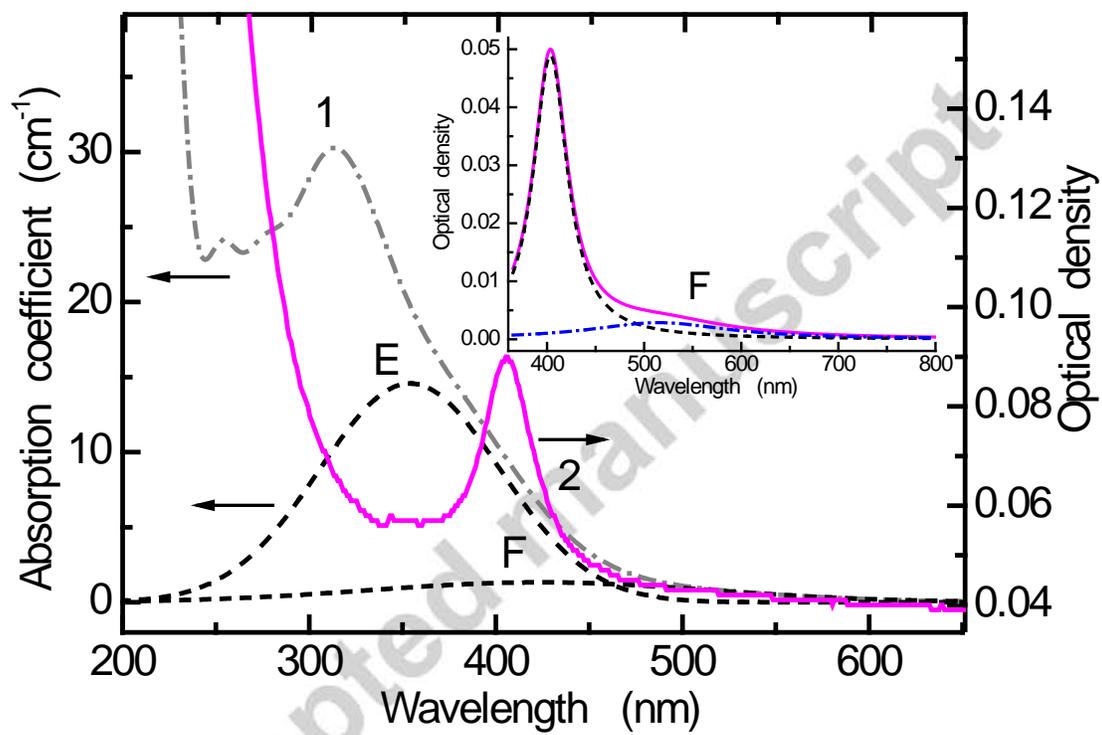
Doses (Gy)	Lifetime (ns) @270 nm	Lifetime (ns) @345 nm
1.22	3.31 (79.5%)	5.56 (71.7%)
2.45	2.40 (55.7%)	5.44 (76.8%)
7.35	6.32 (63.3%)	5.67 (73.0%)
12.2	6.38 (62.0%)	5.71 (72.6%)
24.5	6.15 (63.8%)	5.63 (75.7%)

Figure



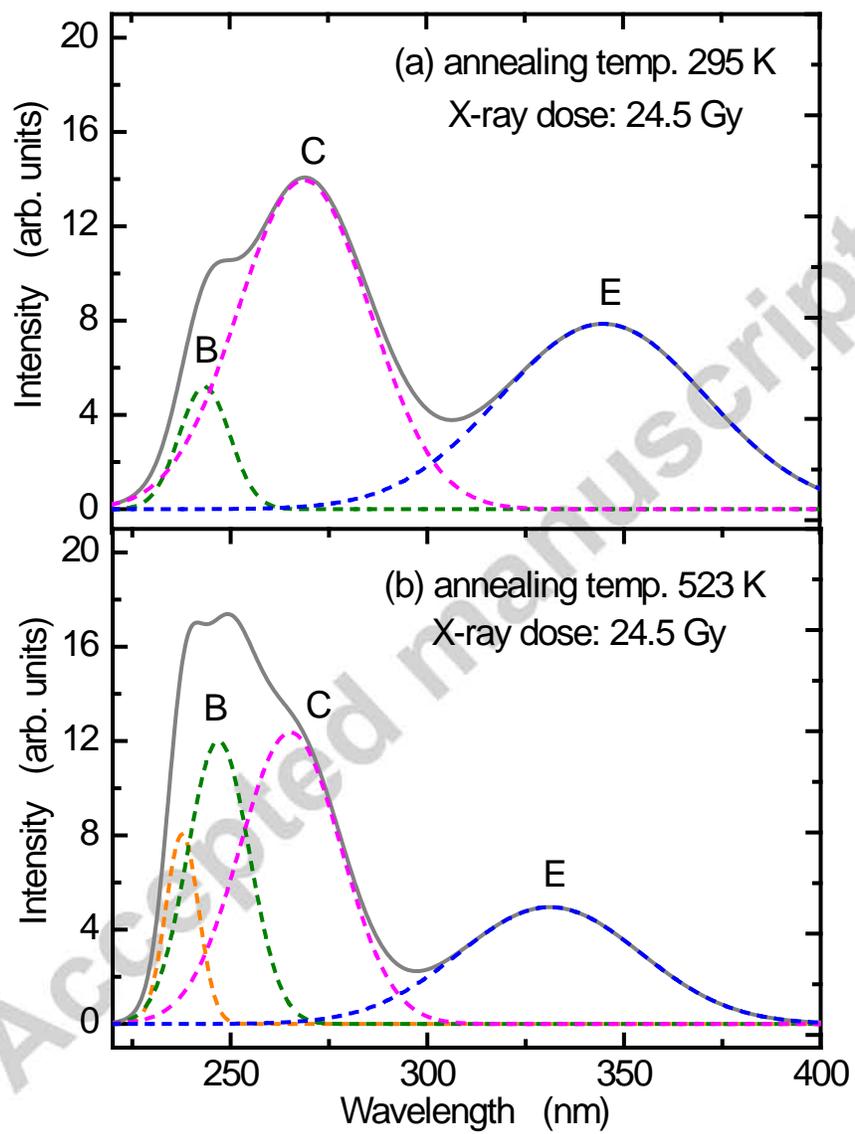
W. Zheng

Fig. 1 (a), (b), (c), (d)



W. Zheng

Fig. 2



W. Zheng

Fig. 3 (a), (b)

