A comparison of different spectra deconvolution methods used in EPR dosimetry with Gorilla® Glasses

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Abstract. Two different spectra deconvolution methods have been compared on samples of Gorilla® Glass (GG) irradiated in the dose range 0-20 Gy and measured with X-band EPR. The first method used a matrix deconvolution procedure using sample-specific sets of reference signals. The second method used a ‘universal’ set of eight reference signals (due to five electron centers, two hole centers and a background) to fit EPR spectra from any GG sample. Dose-responses curves were constructed for each individual reference signal. These were then used to test reconstruction of a laboratory-administered dose of 2 Gy. For the matrix method, the values of the reconstructed and nominal doses were within ±20 % after averaging measurements from three aliquots of each sample. For the universal method, the most promising results were obtained with E1, E4 and H1 signals. The fitting failed for one sample, due to dominance of the background signal.

1. Introduction

Many different glasses demonstrate Electron Paramagnetic Resonance (EPR) signals after exposure to ionizing radiation and therefore may be used as retrospective dosimeters. Several different EPR centers have been reported in the literature. The non-bridging oxygen hole center (OHC) at g=2.01 was observed from samples of window glass(1,2) and commercial glasses(3-4). Boron-oxygen hole centers (BOHC) at g1=2.003, g2=2.012 and g3=2.036 have been observed in irradiated borate and boro-silicate(5-6). The latter usually appear as five lines split by interaction with 11B with a splitting constant of about 1.4 mT. In many publications, complex EPR spectra were observed in glasses after irradiation. Boizot et al.(7) studied some nuclear glasses and detected several different paramagnetic centers, including BOHC, a hole center near alkaline ions (g1=2.0023, g2=2.0088, g3=2.0213), an electron center (gave=2.0011) and a silicon hole center (a broad signal between g=2.00 and g=2.03). Four different defects were described by Le Gac et al.(8) for aluminosilicate glasses, namely the silicon OHC (four such centers around g=2.01), the aluminum OHC (a broad signal between g=2.00 and g=2.035), a trapped-electron center (with g1=1.937 and g2=g3=1.973) and an isotropic electron center at g=1.9992. Five main patterns of EPR spectra were observed for different types of LCD display glass by Trompier et al.(9). Although g-factor values were not presented in the latter work (making direct comparison with signals from other glasses difficult), in other works by the same team(10-11), one observed signal was similar to that from the OHC and another to that from the BOHC. Most of the tested LCD glasses also demonstrated a complex, broad and stable background signal (BG) at g=2.0024. Protective screens from modern touchscreen smartphones (usually made from a special, chemically strengthened glass like Gorilla® Glass (GG) developed by Corning Inc.(12)) demonstrate even greater complexity for both the BG and the radiation-induced EPR signals (RIS). Wieser et al.(13) reported eight possible different signals in such glass (one BG, two hole and five electron centers). Sholom and McKeever(14) also observed many different patterns for RIS as well as for BG signals in GG samples. Recently, at least three different hole centers (OHC, BOHC and the one at g=2.02) and a variety of overlapping electron centers have been reported by McKeever et al.(15). The latter authors also suggest that the origin of the strong BG signals observed in some GG samples is a UV treatment, which is applied to the glasses during phone manufacture to cure the adhesive between the glass layers and the phone. This may explain the significant discrepancy between reconstructed and nominal doses observed by some participants in the last intercomparison(16) in which samples from different parts of the screens from the same brand of smartphones was used.

In general, EPR spectra of GG samples consist of several BG and RIS signals. To estimate correctly the contribution of each individual signal to the overall spectrum it is necessary to apply deconvolution procedures, which are not trivial due to the strong overlap of the signals. In the present study, two methods of spectra deconvolution(13,17) were compared for several GG samples chosen for their different EPR spectra.

1. Materials and Methods

Six Gorilla® glass samples with quite different patterns of EPR signal were selected from more than 100 samples. The six selected samples were from phones Samsung S3, iPhone 6S, a replacement screen for iPhone 5, Samsung Note 3 #1 (with high BG signal), Samsung Note 3 #2 (with low BG signal) and a GG 3 sample from Stemmerich, Inc. Twelve 5.5 x 5.5 mm2 aliquots were cut from each glass sample using a Buehler Isomet 1000 low-speed saw equipped with a diamond blade. EPR measurements were conducted on an X-band Bruker EMX spectrometer with a Bruker ER 4119HS resonator using an 8 mm in diameter sample tube. The parameters of spectra acquisition were: 27 mW microwave power; 0.15 mT modulation amplitude; 10 mT sweep width; 345 mT central field; 81.9 ms conversion time; time constant 163.8 ms; number of scans 10. A Bruker ER 4119HS-2100 reference sample at g=1.9800 was used for g-factor calibration of spectra.

The samples were exposed to doses 0, 2, 5 and 20 Gy (three aliquots per each dose) using a 90Sr/90Y beta source with a dose rate 250 mGy/s; all doses are referred to water. EPR spectra were recorded within one hour of exposure. All spectra were normalized by the mass of the corresponding aliquot.

Two spectra deconvolution methods were used. The matrix deconvolution method requires two reference signals (a background and a dosimetric signal, BG and DS) for each specific phone model/brand. The spectra from unirradiated aliquots of each sample were used as the BG reference signal while the corresponding DS reference signals were obtained as the difference between the spectra measured after a 20 Gy irradiation and the spectra of the unirradiated samples. The second, ‘universal’ deconvolution method used eight reference signals corresponding to specific electron and hole centers, and a BG signal, as described by Wieser et al.(13). The reference signals were developed using the GG from phones Samsung S5830, HTC Wildfire and Nokia X6, with comparable background, light and gamma induced signals.

1. RESULTS AND DISCUSSION
	1. Reference signals used for spectra deconvolution

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Figure 1 shows reference signals used in the matrix deconvolution method. Plot (a) represents the BG reference spectra while plot (b) shows the DS spectra. It should be noted that despite the significant difference in BG signal intensity between Note 3 #1 and #2, the DS spectra in these two samples were quite comparable.



(a)



(b)

Figure 1. BG (a) and DS (b) reference spectra used in the matrix deconvolution method. The BG signal for a Samsung Note 3 #1 was multiplied by a factor 0.2 for clarity. “Raw” next to GG means that this glass was obtained directly from Stemmerich, Inc. and has not received any treatment specific to phone manufacture (e.g. possible treatment with UV light).

Figure 2 demonstrates the reference signals used in the universal method. The BG reference signal was recorded from an unexposed sample one day after sample preparation; signals due to hole (H1, H2) and electron (E1-E5) centers were isolated using EPR spectra recorded after different combinations of gamma dose and light (both visible and ultraviolet) exposures(13). From the experimental spectra the spectral parameters shown in Table 1 were determined and these were then used to simulate the component spectra used in the deconvolution. dHppi in this table is the width of the corresponding gi component of the signal. It should be noted that for H1 and H2 hole centers a hyperfine splitting on three hydrogen atoms was supposed and the corresponding splitting parameter A=0.15 mT was used for simulation of the reference signals. The E1, H1 and H2 were only sensitive to gamma radiation, and the E2 and E5 only to UV light exposure. The E3 and E4 were sensitive to both, gamma and UV exposure, but were only short living (decay time 6 days).



Figure 2. Reference signals used in the universal deconvolution method. See details in the main text.

Table 1. Parameters of the centers that were detected in the sample of a Samsung GG and used for simulation of corresponding reference signals.

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| Center | g1 | g2 | g3 | dHpp1, mT | dHpp2, mT | dHpp3, mT |
| H1 | 2.0141 | 2.0111 | 2.0052 | 0.25 | 0.3 | 0.17 |
| H2 | 2.0188 | 2.0160 | 2.0082 | 0.6 | 0.5 | 0.25 |
| E1 | 1.9849 | 1.9883 | 1.9985 | 0.47 | 0.59 | 0.35 |
| E2 | 1.9839 | 1.9873 | 1.9990 | 0.45 | 0.52 | 0.35 |
| E3 | 1.9801 | 1.9801 | 1.9906 | 0.45 | 0.45 | 0.45 |
| E4 | 1.9904 | 1.9953 | 2.0020 | 0.65 | 0.83 | 0.58 |
| E5 | 1.9967 | 2.0016 | 2.0060 | 0.7 | 0.7 | 0.45 |

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* 1. Examples of spectra deconvolution using matrix and universal methods

Figure 3 shows the matrix deconvolution for samples exposed to 5 Gy. Four lines are shown for each sample, namely the net fit (for 5 Gy) and, separately, the contributions to this fit from the BG and DS reference signals. Good coincidence between the original and fitted spectra are observed for all samples.

Figure 4 shows deconvolution for the same samples using the universal method. Only five of six samples are shown because decomposition for one sample (the replacement glass for an iPhone 5) failed due to its special BG signal. For the replacement glass, the BG was much stronger than the radiation induced components and was very different from the BGs of the other samples and the universal BG signal (see Fig. 1a and Fig.2). The best fitting was obtained for either the Samsung glasses with low BG signals (i.e. Samsung S3 and Samsung Note 3 #2) or the raw GG (GG 3 from Stemmerich, Inc.). This may indicate that in case of strong and dominant BG signal, correct knowledge of the BG is important for quality of fitting.

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Figure 3. Examples of deconvolution for 5 Gy-irradiated samples using the matrix method.

* 1. Dose response curves and reconstruction of a 2-Gy laboratory dose

Typical dose responses are shown in Figure 5 for an example of a Samsung S3 glass. For the matrix method, the DS increases with dose and all samples demonstrate a linear dose response intersecting the y-axis at zero. For the universal method, the dose response for the different components depends on the sample. For example, in the case of the Samsung S3 phone, the signals due to the E1, E4 and H1 centers were prominent and dose dependent. The E4 center is only short living, but was recognized here because measurements were made within one hour after irradiation. Some samples demonstrated a relatively high contribution of some reference signals to the zero-dose spectra. This could be related to possible UV treatment of the protective glass during phone manufacture.

Doses of 2 Gy were reconstructed using curves similar to shown in Fig. 5. The results are presented in Table 2. It is seen that for the matrix method the reconstructed doses coincide with the nominal value within ±20 %; for the universal method a similar deviation was observed for all samples except for Note 3 #1. In general, the best results with this method were obtained using E1, E4 and H1 centers, when present.

Such level of uncertainties is comparable with that of most existing emergency dosimetry techniques(18). It should be noted that above uncertainties were obtained for samples measured soon after irradiation and stored at controlled conditions between exposure and measurement. For accidentally irradiated samples that were stored in realistic conditions between irradiation and measurement, one can expect the higher level of uncertainties due to influence of environmental factors like sunlight, temperature etc, but study of these factors was out of the goals of this work.

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Figure 4. Examples of deconvolution for 5 Gy-irradiated samples using the universal method.

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Figure 5. Examples of dose responses observed for a Samsung S3 glass. (a) is the response obtained with the matrix method while (b) is the set of curves obtained with the universal method for those signals that demonstrated an increase with dose (E1, E4 and H1 for this specific glass).

Table 2. Results of dose reconstruction for 2-Gy samples obtained with matrix and universal method.

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| Sample  | Matrix method, aver ±std, Gy | Universal method, Gy |
| Note 3 #1 | 1.69 ± 1.37  | 3.16 (E4), 3.03 (H2) |
| Note 3 #2 | 2.32 ± 0.17  | 2.21 (E1), 2.21 (E4), 6.03 (H1) |
| Samsung 3 | 1.65 ±0.49  | 2.39 (E1), 2.00 (E4), 2.66 (H1) |
| iPhone 6S | 1.83 ± 0.50 | 2.68 (E4), 2.17 (E5) |
| GG 3 | 2.20 ±0.21 | 3.08 (E1), 2.12 (E4), 2.37 (E5), 2.30 (H1) |
| iPhone 5 (replacement) | 2.40 ± 0.70  | N/a |

1. ConclusionS

Both tested methods demonstrated the ability to isolate radiation-induced signals from the EPR spectra of irradiated GG samples and to use them to reconstruct doses with uncertainties of about ±20 % at the 2-Gy level. The matrix method may be applied to any glass providing that reference DS and BG signals were obtained for such glass in advance. The universal method does not require sample-specific reference signals, but may require updated BG reference for some glasses if the actual BG spectrum is quite different from the universal BG reference. Future work may be related to testing the methods on samples stored in conditions that are similar to some realistic scenarios (e.g., irradiated and measured at different times after irradiation with different indoor/outdoor light exposures between irradiation and measurement).

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