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Role of Afterglow in Optically Stimulated Luminescence of YAP:Mn

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The afterglow of the $YAlO_3:Mn^{2+}$ single crystals irradiated with X-rays (45 kV, 0.3 mA) is studied to understand its role in the behavior of the optically stimulated luminescence, which is observed during pulsed stimulation with blue light (470 nm) of a pre-irradiated crystal. In non-irradiated crystal the same light does not have this effect. It is shown that long lasting afterglow and optically stimulated luminescence response follow the hyperbolic kinetics with the power in denominator less than one. It confirms the common nature of both phenomena, which is likely explained by the presence of several types of defects in the studied crystal, competing in trapping/re-trapping and releasing the carriers during the irradiation and relaxation. On the other hand, it was find out that the initial part of optically stimulated response demonstrates exponentials relaxation. A technique which uses the revealed peculiarity is proposed and tested to determine the absorbed dose of irradiation from the optically-stimulated luminescence in $YAlO_3:Mn^{2+}$ crystal.

topics: $YAlO_3:Mn^{2+}$ (YAP:Mn), afterglow, optically stimulated luminescence, Becquerel decay function

1. Introduction

Yttrium aluminum perovskite doped with Mn^{2+} ($YAlO_3:Mn^{2+}$ or YAP:Mn crystal) is considered to be a prospective material for luminescence dosimetry because of the appearance of intense thermoluminescence (TL) with the main TL peak at about 200°C after irradiation by ionizing radiation [1, 2] and because of possibility to readout an optically-stimulated luminescence (OSL) response [3, 4]. Its advantages consist of a very high radiation resistivity, chemical stability, mechanical strength, weak fading, high sensitivity and high energy response [1, 2, 5]. Its dosimetric properties are studied mainly for usage in the TL dosimetry [1, 2, 5, 6], however, peculiarities of the OSL phenomenon in this material as well as its application for estimation of the absorbed dose are not yet well understood. The OSL glow as well as TL at 200°C appear in a wide green band with a maximum near 530 nm and is connected with Mn^{2+} intra-center transitions [4]. It means that it could be accompanied by photoluminescence (PL) of Mn^{2+} ions if the stimulation light excites them. Fortunately, it was revealed in [4] that the decay of OSL glow is much longer than the PL life time being equal to 3.5 ms. Based on the results reported in [4], the OSL response of the irradiated YAP:Mn^{2+} have been studied by means of the time-resolved OSL readout with a pulse stimulation at 470 nm using a setup described in [6]. These experiments revealed that the OSL glow lasts for a long time after termination of the stimulation pulse and when measured precisely in a wide photometric dynamic range during several hundreds of seconds, demonstrates glow kinetics that differs from the exponential relaxation predicted for the simplest model of the OSL phenomena [7, 8]. The decay of the OSL glow initiated by pulse stimulation (100 ms) with blue light (470 nm) is shown in Fig. 1 [9]. It cannot be fitted even by few exponents but it is well described by a generalized hyperbola, which is known also as an empirical Becquerel decay function [10, 11]. The function is expressed as

$$I(t) = \frac{I(0)}{(1 + w\,t)^{\alpha}}, \tag{1}$$

where w and α are parameters of the hyperbola. The special techniques of nonlinearity correction of photon-counting, dark count subtraction and application of an adaptive counting bin allowed to extend the dynamic range for at least one order in the

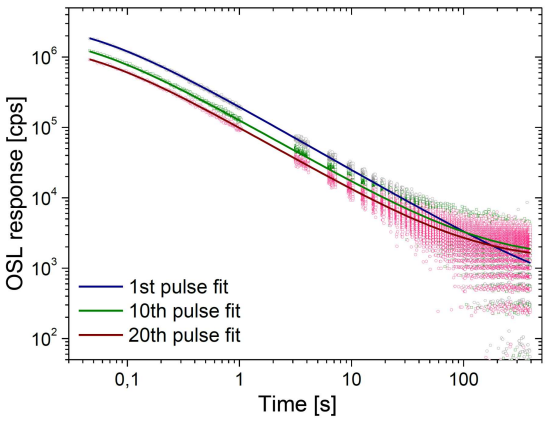

Fig. 1. The YAP:Mn OSL decay curves (points) recorded after the 1st (violet), 10th (olive) and 20th (purple) sequential pulses of 100 ms duration of blue (470 nm) light stimulation together with their fits (solid lines) by mean of function (1) with some background from [9]. The repetition period of stimulation pulses was equal to 420 s.

photometric scale, register the OSL response above the noise level after 2 Gy dose of X-ray irradiation for up to 10^4 s [12]. It was confirmed that the OSL decay kinetics is described by (1) with high accuracy because the coefficient of determination (adjusted R^2) of the Becquerel decay function for fitting of the experimental data exceeded 0.999.

Although the experiments conducted in [12] show the ability to confidently register the YAP:Mn OSL response from the absorbed dose of 0.1 mGy from the ^{137}Cs source, however, it was not possible to unambiguously link the parameters of this response with the absorbed dose.

One can point out at least two reasons of difficulties with estimation of the absorbed dose from the OSL response of the YAP:Mn crystal. The first is caused by the fact that the α parameter of hyperbola in the denominator is less than one. The value of parameter $\alpha = 0.85 \pm 6 \times 10^{-4}$ found in [12] makes the function (1) a non-integrable one. If we interpret the integral of the luminescence glow function as the sum of the dosimetric response, like in the case of the TL dependence upon temperature, then the non-integrability (1) will formally mean the infinity of the total intensity of light, which, of course, cannot be considered an adequate interpretation. The second consists of a complicated character of OSL response transformation in a stimulation pulse series. Although the kinetics of responses to repeated stimulation pulses are similar (see Fig. 1) and each subsequent pulse decreases the response intensity due to the gradual decrease of the number of filled dosimetric traps, it is noticeable that the luminescence intensity level at the end of the response slightly increases with increasing the number of stimulation pulses. It is revealed as an increasing background component in the fitting procedure. This suggests that there are at least two processes contributing to the YAP:Mn OSL response, different speed of which distort the response in its temporal evolution. The slow one cannot be completed during the recording of the OSL response and causes accumulation of glow intensity. The last is only observed when the fast process intensity becomes small enough. One can suppose that the slower process is connected to the shallow traps, which are usually empty at room temperature, but can re-trap charge carriers released from metastable dosimetric traps by optical stimulation and slow down the relaxation of excited states. The role of deeper traps is also not excluded. The influence of competing shallow traps on TL and OSL dosimetry is not a new topic in the study of dosimetric phosphors and has been discussed previously [8, 13–18], but the known data hardly fit the case of OSL in YAP:Mn, which is yet poorly studied in this context.

The present work is devoted to further investigation of the OSL peculiarities in YAP:Mn crystals aimed for a deeper understanding. In particular, it is aimed at exploring the role of phosphorescence, being observed usually as an afterglow of irradiated phosphors, in the formation of OSL response, as well as for finding a way to estimate the absorbed dose of ionizing radiation from the measured OSL response.

2. Experimental

Single crystals of YAP:Mn with nominal composition $Y_{1.02}Al_{0.98}O_3$:Mn(0.05%), Hf(0.2%) (CZ#31) were grown by the Czochralski method (see [19] for details). The samples in the form of plates with dimensions $3 \times 3 \times 1$ mm^3 cut from the single crystal by diamond saw without polishing of surfaces were used for the measurements. The X-ray produced an afterglow and the OSL response of the irradiated samples were measured using the setup and experimental technique described in [6, 12]. The adaptive photon-counting bin was used with duration (time interval of photon-counting) extended by a lower rate of intensity decay. Measurements of long glow decay were performed in fragments over several days without removing the sample from the cell of the setup. The samples were irradiated by X-ray tube with voltage 45 kV and current 0.3 mA. The exposure time was in the range from 2 s to 1000 s and was controlled by an automated shutter. It was established by the TL response intensity that such irradiations correspond to absorbed doses in the range from 60 mGy to 30 Gy. The time delay after the end of irradiation to the start of the afterglow registration was measured by a stopwatch with an accuracy of 1 s. The residual signal was removed by annealing of the sample before irradiation at temperature 400°C in air. The OSL measurements were being performed when the afterglow intensity was less than 1000 photons per second [cps]. The nonlinear fitting by means of the Savitsky–Marquardt

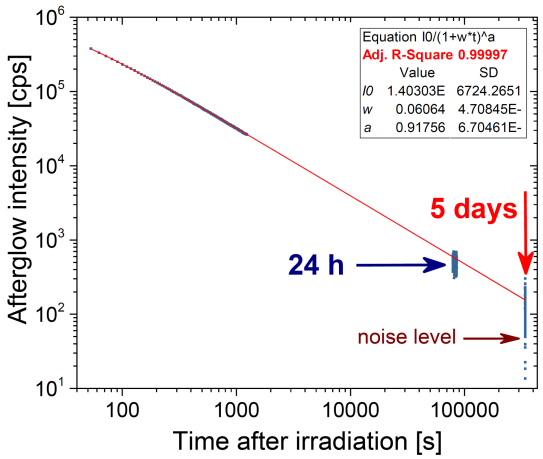

Fig. 2. The kinetics of green afterglow (points) of YAP:Mn crystal induced by the X-ray irradiation during 30 s (absorbed dose about 0.9 Gy) and its fitting (solid line) by the function (1). The inset represents the parameters of fitted function.

method was used for the experimental data approximation. The application of the adaptive photon-counting bin was considered as a weighting method at nonlinear regression and no additional weighting was used for the experimental data fitting.

3. Results and discussion

The typical afterglow decay kinetics after X-ray irradiation of YAP:Mn crystal is shown in Fig. 2. The afterglow can be measured for several days, even after exposure for 30 s. As can be seen, in Fig. 2, the X-ray produced afterglow has the same shape as the OSL response after a single stimulation pulse presented in Fig. 1 and in [12] and cannot be satisfactorily fitted by any other simple function besides that given by (1). In the last case, the coefficient of determination (or adjusted R^2) of the fit by the Becquerel decay function (1) in a wide range of time and glow intensity reaches the value more than 0.9999. This indicates a very high correspondence of this model to experimental data. It should be emphasized that the blue light with wavelength 470 nm used in our experiments for OSL stimulation does not cause afterglow nor the OSL signal if the YAP:Mn crystal has not been irradiated before.

The X-ray produced afterglow measurements were started with some delay after ending of irradiation exposure, which was required to move the sample from the place of irradiation to the luminescence measurement setup. To take it into account, the expression (1) has to be modified to the form

$$I(t) = \frac{I(0)}{\left(1 + w\left(\Delta t + t\right)\right)^{\alpha}}, \qquad (2)$$

where Δt is the time delay between the irradiation end and the start of the measurement, while variable t describes the time after the measurement has started. The X-ray produced afterglow curves after different doses (X-ray exposure times) are shown in Fig. 3. When the parameter Δt is considered as an additional free parameter of approximation, then its value found from fitting by the function (2) coincided with that value measured directly by stopwatch with accuracy better than 1 s in most experiments shown in Fig. 3. This is another confirmation of the adequacy of the model (2) to the experimental observations. Next, the determined value Δt was fixed as a constant to find a better fitting of other parameters of (2). All experimental dependencies in Fig. 3 are fitted by the function (2) with the adjusted $R^2 > 0.999$.

The initial intensity of the afterglow can be found from such fitting procedure regardless of the delay Δt. The dependence of the intensity on the X-ray exposure time, shown in Fig. 4, demonstrates a trend to saturation at the irradiation time close to and longer than 300 s and can be described by a simple model $I = I_{0,\mathrm{sat}}\,(1-\exp(-t/\tau))$, where the found parameter τ is equal to 98 s.

The afterglow induced by X-ray irradiation studied here and the long-time decay of OSL response produced by blue light (470 nm) stimulation studied in the same YAP:Mn crystal before [6, 9, 12] (compare Fig. 2 with Fig. 1 in the present work of with Fig. 7 in [12]) reveal the same main peculiarities of their behaviour, and hence the common nature of these phenomena. It should mean that the complexity of the OSL response in YAP:Mn crystal is caused by the same reasons and mechanisms that explain the hyperbola kinetics of phosphorescence in other phosphors [11] which is also very common but less studied in recently popular long-persistent phosphors [20–23]. Following the conclusion of the analysis on the Becquerel type kinetics of phosphorescence with $\alpha < 1$ [11], the reasons for such behaviour are the presence of several traps delivering carriers to recombination centers or re-trapping on dosimetric traps of those carriers which are released or tunneled from even deeper traps. Such interpretation coincides with studies of YAP:Mn crystals demonstrating, next to the main dosimetric TL peak at 200°C, an additional peak at 350°C attributed to the unintentional dopants of Mn^{4+} and Cr^{3+} (see [24] for details). It can also be noted that the change in the w parameter with the irradiation time (see insets in Fig. 3) is also a feature of the Becquerel type phosphorescence kinetics with $\alpha < 1$ [11]. From this point of view, the uncertainty of interrelation of the OSL response parameters becomes more understandable, and the absorbed dose of preliminary irradiation of the crystal is explained by additional uncontrolled factors influencing their interdependence, which should be controlled for application of YAP:Mn in OSL dosimetry.

One of the suggestions to be checked is that the rapid recombination of carriers just released from dosimetric traps may occur locally in close vicinity of the recombination center. Slower processes related herewith to the diffusion of carriers or excited

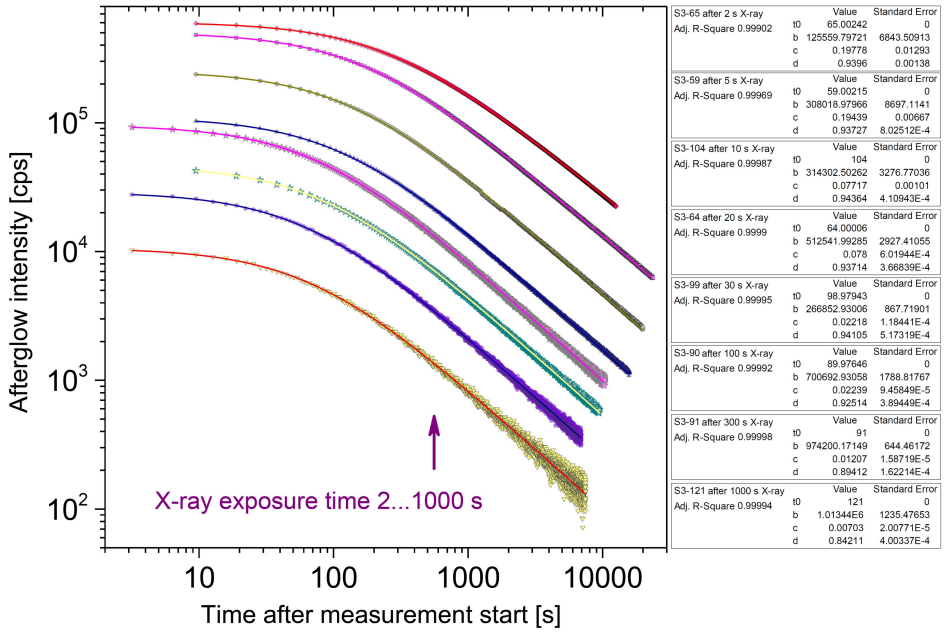

Fig. 3. The X-ray produced afterglow (points) of YAP:Mn crystal after different irradiation times and the corresponding fitted dependencies (solid line) in the form of (2). The inset represents the parameters of fitted functions. The last number in the sample notation (S3-##) shows the time delay Δt [s] from the end of irradiation till start of measurement. Other notations represent the values in (2): t0 —Δt, b — $I(0)$, c — w, d — α.

states through the crystal should less influence the luminescence emission at the initial moment of optical stimulation of the irradiated crystal. That is why our further experiments were performed with periodic stimulation by short pulses of 10 ms duration and readout of the OSL intensity by means of photon-counting in bins (channels) with a duration of 2 ms. The results of experiments with pulses' repetition periods 1 and 9 s are shown in Fig. 5a and b, respectively. Because of the short stimulation and short counting channels, the registered signal is rather noisy. To decrease its dispersion, the registered intensities in the same time channels were averaged over several sequential pulses. One can see that, in the case of a short repetition period of stimulation, the initial part of glow relaxation remains almost constant on the first several stimulation pulses, but its posterior part immediately begins to elevate in spite of expectation that the signal will drop with increasing the number of pulses. It occurs because the slower process cannot end between the sequential stimulation pulses and leads to the accumulation of glow intensity. When the period of stimulation pulses becomes 9 s one cannot observe lifting of any part of the signal and it drops slowly keeping the same shape.

If rapid relaxation in the first moments after stimulation is a direct recombination of released carriers in the vicinity of the recombination centers, it can have different kinetics from the kinetics of the rest of the glow curve. The next step was to study the behaviour of only the initial part of glow relaxation stimulated by multiple repeated, short pulses. Such

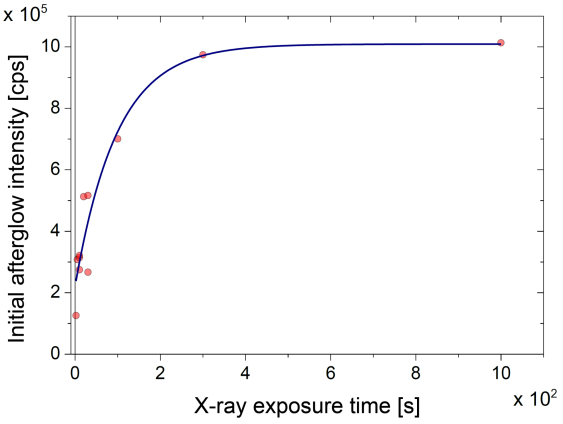

Fig. 4. Dependence of the initial afterglow intensity upon the X-ray exposure time. The solid line represents an approximation of experimental points by the function.

initial OSL signal was registered as photon-counting in the first 50 ms after the stimulation pulse and used further as a sample of the response corresponding to each stimulation pulse. The dependencies obtained for different duration of X-ray irradiation of YAP:Mn crystal in the range from 2 till 30 s are presented in Fig. 6 with the fitted curves of exponential relaxation. Except for the variable dependence of glow intensity, some constant bias of the obtained signal can be attributed to a long-lasting component of the response that looks like a constant in a short time scale.

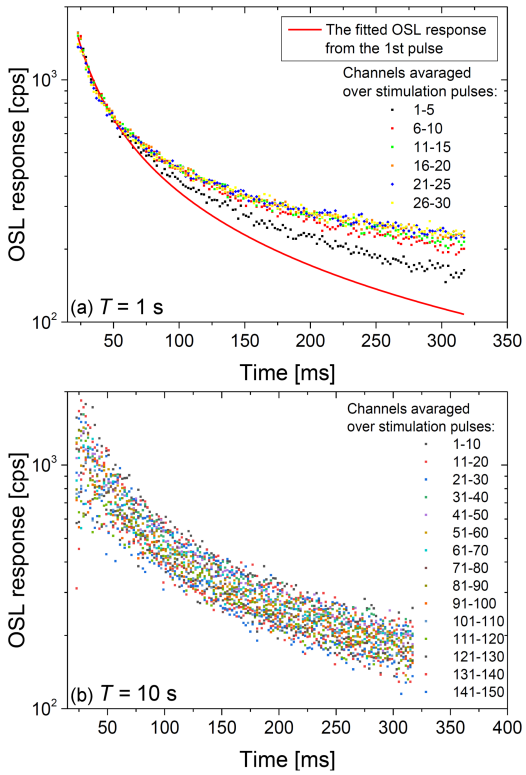

Fig. 5. The OSL response of the YAP:Mn crystal on the blue light (470 nm) stimulation by pulses of 10 ms duration registered as photon-counting in the channels of 2 ms duration at pulses repetition period 1 s (a) and 9 s (b).

As it was mentioned before, the simplest OSL kinetics model is exponential relaxation in the form

$$I_{\mathrm{OSL}}(t) = I_{\mathrm{OSL}}(0)\,\exp\left(-\frac{t}{\tau}\right), \qquad (3)$$

where τ is the relaxation time and variable t has a meaning of the total stimulation time, although formally both τ and t can be defined in terms of the number of stimulation pulses. However, because of the high dispersion of photon-counting for low-intensity signals, it is difficult to prove the type of kinetics especially for low doses of irradiation. For example, the coefficient of determination (adj. R^2) of the data on the 2 s X-ray exposure is equal to 0.5 for the exponential relaxation function (3) (see inset in Fig. 6a) and the Becquerel hyperbola (1). That is why to check the suggestion about exponential relaxation of the rapid component of the OSL response, we used the property of the exponential function to remain the same after differentiation or integration. The integration of (3) with appropriate initial conditions gives the model for the integrated OSL intensity, i.e.,

$$S_{\mathrm{OSL}}(t) = \tau\, I_{\mathrm{OSL}}(0)\,\left(1-\exp\left(-\frac{t}{\tau}\right)\right). \qquad (4)$$

Corresponding data were prepared from the measured OSL intensity by summation over stimulation pulse number. The constant bias was excluded

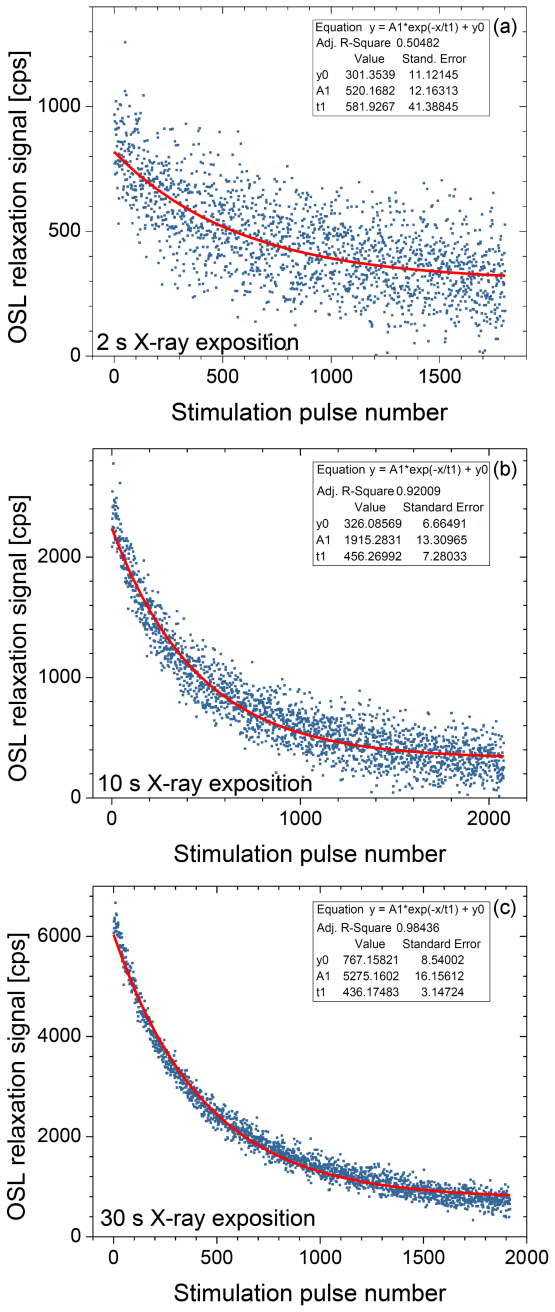

Fig. 6. The dependence of the rapid component of the YAP:Mn OSL response upon stimulation pulse number with repetition period 1 s for the X-ray irradiation during 2 s (*a*), 10 s (*b*) and 30 s (*c*). Experimental data are represented by points and their approximations by the function (3) are drawn by solid line. The insets demonstrate parameters of fitted functions.

from the calculation. The obtained dependencies together with fitted curves are shown in Fig. 7. It is clearly seen that the reliability and confidence of the approximation by the model (4) is much higher, as the coefficient of determination exceeds 0.999 even for the lowest dose. This confirms also the suggestions made above.

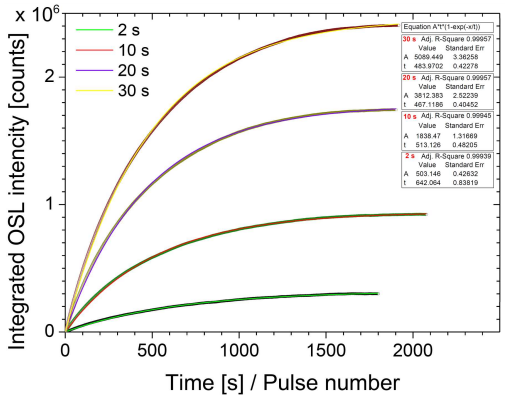

Fig. 7. The integrated rapid component of the OSL response vs pulse number for different X-ray exposure of YAP:Mn crystal. Experimental data are represented by points and their approximations by the function (4) are drawn by solid line. The insets demonstrate parameters of fitted functions.

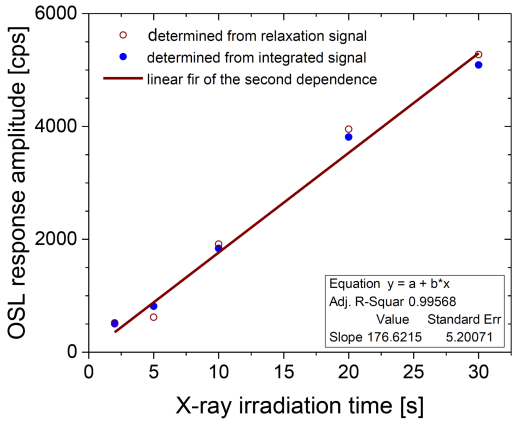

Fig. 8. The dose dependencies of the YAP:Mn crystal OSL response amplitude and the amplitude of the integrated OSL response upon the X-ray exposure time in the range 2–30 s, and linear fit of the last.

The amplitude coefficients both in (3) and (4) can be the measures of the absorbed dose of ionizing radiation after X-ray exposure of the YAP:Mn crystal. The dependence of the corresponding fitting parameters from the time of irradiation, having the meaning of the dose-dependence, is shown in Fig. 8 both for OSL intensity and its integrated value, as well as linear fit of the last. At this, the pulse repetition period in 1 s results in coincidence of numerical scales for both dependences. The linear character of the dose-dependence confirms the applicability of the approach used for the OSL dosimetry based on YAP:Mn crystal.

4. Conclusions

Our investigation of the afterglow caused by the X-ray irradiation of the YAP:Mn single crystal shows the same peculiarities as the long-lasting OSL glow revealed before for the same crystal. In particular, the kinetics of the X-ray produced afterglow and the glow occurring after the blue light stimulation pulse in the preliminary irradiated YAP:Mn obey the hyperbolic law described by the empirical Becquerel decay function with a power in denominator less than one giving a lingering decay. This means that the dominant mechanism of relaxation of the carriers released optically from the dosimetric traps is the same as for the X-ray produced afterglow and is most likely caused by an additional influence of deeper traps in the YAP:Mn crystal. It impedes to determine the absorbed dose from the OSL response.

At the same time, the technique allowing eliminating the influence of the long-lasting afterglow has been proposed. This technique is based on the reading out of the initial part of OSL response only after short stimulation pulses. The OSL signal measured in such a way has decay kinetics different from the long-lasting one and, as it was confirmed, can be described by an exponential relaxation. This technique allowed us to obtain a dose-dependence from the OSL response for the X-ray irradiated YAP:Mn crystals in the range 60–900 mGy.

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