



Synthesis of $\text{MgB}_4\text{O}_7:\text{Dy}^{3+}$ and Thermoluminescent Characteristics at Low Doses of Beta Radiation

O Legorreta-Alba^{1,2}, E Cruz-Zaragoza^{1,*}, D Díaz² and J Marcazzó³¹Institute of Nuclear Sciences, National Autonomous University of Mexico (UNAM), PO Box 70-543, 04510 Mexico City, Mexico²Chemistry Faculty, National Autonomous University of Mexico (UNAM), 3000 Universidad avenue, 04510 Mexico City, México³“Arroyo Seco” Institute of Physics (Uncpba) and Cificen (Uncpba-Cicpba Conicet), Pinto 399, 7000 Tandil, Argentina*Email: ecruz@nucleares.unam.mx

ARTICLE INFORMATION

Received: June 15, 2018
 Revised: July 11, 2018
 Accepted: July 19, 2018

Published online: August 6, 2018

Keywords:

Magnesium tetraborate; Dysprosium;
 Thermoluminescence; Beta-radiation;
 Dosimeter.

DOI: [10.15415/jnp.2018.61012](https://doi.org/10.15415/jnp.2018.61012)

ABSTRACT

The synthesis and thermoluminescent characteristics of dysprosium-doped MgB_4O_7 are analyzed. The phosphor at different concentrations (0, 0.1, 0.5, 1, 2 and 4 mol%) of the dopant was prepared by the solution-assisted method. The magnesium borate compound was confirmed by X-ray diffraction. The annealing and dopant concentrations effects on the crystalline matrix were investigated. The highest thermoluminescent sensitivity was found with 450°C of annealing temperature and at high Dy^{3+} concentration too. The un-doped MgB_4O_7 phosphor shows a broad glow curve which peaked at 199°C and about 306 °C. Introducing Dy^{3+} dopant in the matrix that behavior was strongly changed. The wide glow curve shows three glow peaks; two small shoulders at 124 and 195 °C, and a highest peak between 323 and 336 °C temperature range. A large linear dose-response (5 – 2000 mGy) beta dose was obtained. The complex glow curves were deconvolved and the kinetics parameters were determined considering the general order kinetics model.

1. Introduction

Alkali earth ions such as Li, Zn, Sr, Ca, and Mg based on tetraborate compound have been considered as important luminescent materials because of their excellent thermal and chemical stability, simple synthesis and cheap reagent material [1-8]. In particular, the MgB_4O_7 phosphor is attractive due to its low effective atomic number ($Z_{\text{eff}} = 8.4$) close to that of soft biological tissue ($Z_{\text{eff}} = 7.42$) and less value than that of the compact bone ($Z_{\text{eff}} = 13.59$), which implies a small photon energy dependence [9-10]. However, the un-doped magnesium borate has a low thermoluminescent (TL) sensitivity. Due to this disadvantage, MgB_4O_7 has been doped with different trivalent ions mainly of rare earths such as Gd, Ce, Tm, Nd, Dy, Eu, Ho [11-16], since it is known that the addition of small amounts of activators with another charge number of valence [9, 17-18] may increase the concentration of imperfections that are important factors improving the TL property of the host matrix. Special attention has been given to the TL study of Dy^{3+} doped MgB_4O_7 [5,18]. From the first studies of this phosphor material, carried out by Hitomi *et al.* [7,19], considerable effort has been devoted to improves its TL properties. In different works [5, 10, 15, 20-21], it has been reported that

$\text{MgB}_4\text{O}_7:\text{Dy}^{3+}$ in addition being a material closely equivalent to the soft biological tissue presents a high sensitivity, a single thermoluminescent peak at about 200 °C, with linearity in the dose-response curve over a wide range of doses, good reproducibility and low fading of the TL signal. Currently, the works related to $\text{MgB}_4\text{O}_7:\text{Dy}^{3+}$ focused on evaluating the optimal conditions of a highly sensitive materials [22], also have been leaning to the determination of the influence of their structural characteristics [23]. In this sense, knowing that the TL characteristics of the magnesium borate material are determined by its preparation method [5, 17, 23–24], in this work the TL characteristics of $\text{MgB}_4\text{O}_7:\text{Dy}^{3+}$ were obtained by the, scarcely known, solution-assisted method.

2. Experimental Procedure

MgB_4O_7 was synthesized by solution-assisted method and appropriate amounts of dysprosium dopant was added to the phosphor to obtain different concentrations (0, 0.1, 0.5, 1.0, 2.0 and 4.0 mol%). The reagents material for obtaining the magnesium borate crystalline matrix were $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.999%) and $(\text{NH}_4)_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ (99%), both of Sigma-Aldrich brand. On the other hand, the

impurity was introduced in the MgB_4O_7 matrix by using as react dysprosium nitrate, $\text{Dy}(\text{NO}_3)_3$ (99.9%), from Sigma-Aldrich brand. The reagents, in suitable stoichiometric amounts, were dissolved and stirred in the deionized water. Subsequently, the solvent was evaporated and the resulting solid was placed in an alumina crucible which was sintered at 800°C for 2 h. The molten mass was then cooled to room temperature, crushed and sieved. Finally, a series of dysprosium doped MgB_4O_7 samples batches was considered for all measurements.

Formation of the crystalline compound in powder form was determined by analysis the X-ray diffraction. The diffractogram was carried out in a Bruker Phaser D2 diffractometer and considering the range from 10° to 55° in the Bragg angle (2θ), using an angular rate counting of $0.02^\circ/\text{s}$. This apparatus was equipped with a Ni filter and Cu-anode X-ray tube operating with 30 kV and 10 mA. The samples were attached on a Bruker AXS Si-Einkristalle sample holder. Thermoluminescence of the phosphor samples were measured on double aliquots and by using a Harshaw model 3500 TLD reader. Each sample was weighted with 8.0 ± 0.1 mg. The thermoluminescent glow curves were obtained at constant heating rate of $2^\circ\text{C}/\text{s}$, from room temperature up to 450°C , and under nitrogen atmosphere to avoid the spurious thermoluminescent signals. The samples were irradiated with β radiation from a $^{90}\text{Sr}/^{90}\text{Y}$ source which provided 0.1099 mGy/s dose rate.

3. Results and Discussion

3.1 X-ray Analysis

Figure 1 shows the X-ray diffraction (XRD) patterns of our host material matrix and from MgB_4O_7 (PDF-00-031-0787) standard. The adjustment between the experimental signals and the diffraction lines from MgB_4O_7 standard makes evident that the crystalline phase of MgB_4O_7 was obtained. This phase corresponding to an orthorhombic crystalline system with lattice parameters of $a_0 = 8.596$ Å, $b_0 = 13.729$ Å, $c_0 = 7.956$ Å and the space group *Pbca*. The diffractograms of the compounds doped with Dy^{3+} revealed the crystalline matrix formation and the absence of signals associated to second phase of dysprosium.

3.3 Dopant Concentration Effects on TL

Figure 3 shows the thermoluminescent (TL) glow curves of un-doped and dysprosium doped MgB_4O_7 with different concentrations of ion impurity. By comparing the glow curves among of them, a drastic change in the shape of the glow curves and their TL intensity occurred when the dysprosium dopant was present in the MgB_4O_7 matrix. The glow curve

of un-doped MgB_4O_7 presents two peaks at 199 and 306°C which can be related to the intrinsic TL emission from the lattice of this compound. However, the thermoluminescence from dysprosium doped MgB_4O_7 with different impurity concentration presents a complex glow curves consisting by a broad glow peak with maximum temperature (T_m) located between 323 and 336°C , and two other peaks of lower intensity about 124 and 195°C widely overlapped to each other. These changes imply that, when the Dy^{3+} is incorporated into the matrix, it originates or improves the activation of other types of traps that participate in the thermoluminescent phenomenon. On the other hand, for 2.0 and 4.0 mol% of dysprosium concentration (as can be seen in Figure 3), the TL peak of higher intensity ($323 - 336^\circ\text{C}$) was strongly increased.

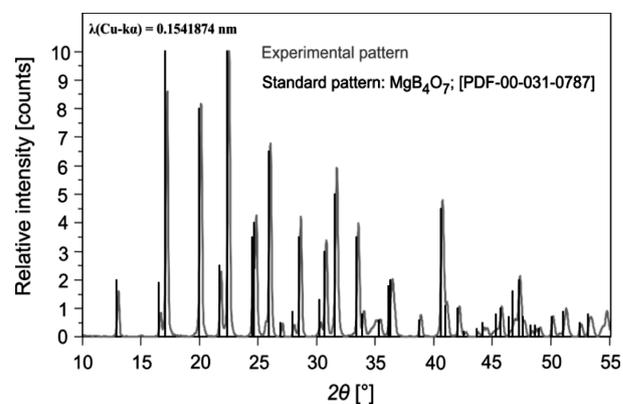


Figure 1. Powder X-ray diffraction of MgB_4O_7 prepared by solution-assisted method (experimental pattern), and the standard powder diffraction lines (*hkl*) corresponding to the PDF-00-031-0787 file.

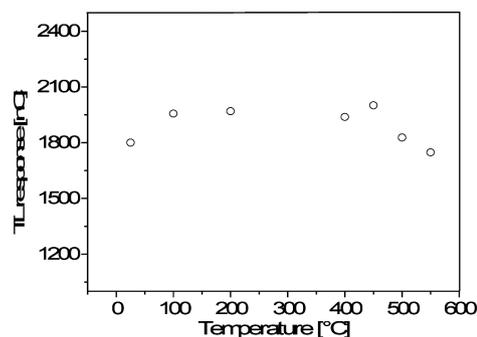


Figure 2. TL response of MgB_4O_7 : Dy^{3+} (4.0 mol%) as a function of the annealing temperature ($100 - 550^\circ\text{C}$). The samples were exposed with 100 mGy dose beta radiation.

The TL intensity was growth as the concentration increases making evident the role of the Dy^{3+} as good activator ion in the magnesium borate optimizing the TL property. However, the fast intensity growth occurs when the impurity concentration increases from 1.0 to 2.0 mol%.

It is important to mention that at higher concentration of dysprosium (4.0 mol%) a TL intensity reduction was not observed, contrary to finding by other authors in MgB_4O_7 :Dy nanophosphor [23]. While at higher concentration (4 mol%) of dysprosium in our MgB_4O_7 samples without annealing temperature, the TL intensity was very slowly increased respect to 2.0 mol% of Dy^{3+} . In that case, may be the dysprosium impurity aggregation occurs in the lattice. That observation also is according to other authors for dysprosium doped borate nanophosphor [23], due to the different ionic radii of the magnesium borate ions (B^{2+} , Mg^{2+} and Dy^{3+}), so the ion impurity due of its larger size cannot replace either of them in the phosphor matrix. In consequence the dysprosium ion at higher concentration, 4.0 mol% in that case without annealing treatment, it can be incorporated as interstitial ions causing their aggregation in the structure matrix.

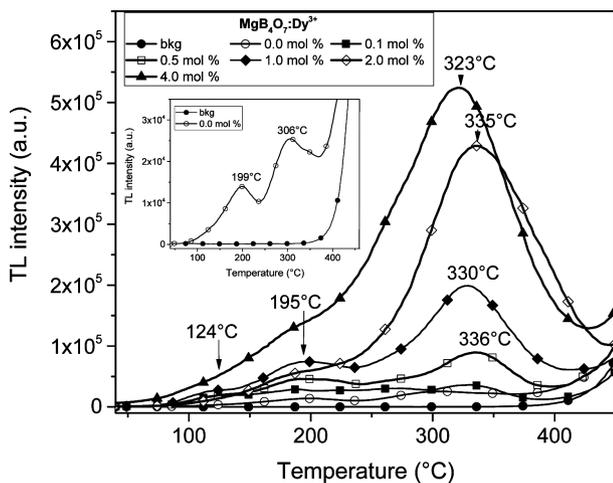


Figure 3. Thermoluminescent glow curves of dysprosium doped MgB_4O_7 and irradiated with 100 mGy. Dopant ion concentration varies as: 0, 0.1, 0.5, 1.0, 2.0, 4.0 mol%. In the inset are the glow curves of the un-doped magnesium tetraborate phosphor and the TL background (bkg) signal.

Due to the higher TL intensity of MgB_4O_7 : Dy^{3+} (4.0 mol%), it was considered for the TL response, i.e., it is an integral under the glow curves. Figure 4 shows the linear TL dose-response in the range from 5 to 2000 mGy. A superlinear stage also was observed, this behavior may be ascribed to the low TL sensitivity of this magnesium borate at low beta doses. However, several types of traps in competition may be included in the recombination process during the TL signal emission producing the superlinear and linear stages, in these cases a deep analysis should be carry out with more details [26-27]. The superlinear stage with a lower growth rate than that of the linear region occurred.

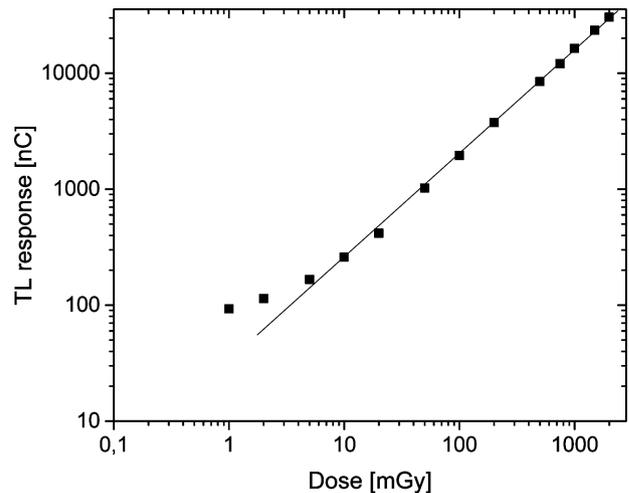


Figure 4. TL dose-response (0.001 – 2 Gy) of MgB_4O_7 :Dy(4.0 mol%) after annealing at 450°C for 30 min. Phosphor samples irradiated with beta radiation.

3.4 Analysis of the Complex Glow Curves by Deconvolution

The structure of the complex glow curves from MgB_4O_7 :Dy(4.0 mol%) was analyzed by the computerized glow curve deconvolution program (CGCD) considering the general order kinetics (GOK) model [24]. The samples were exposed with 1000 mGy beta dose filling the traps levels in the band gap and very clear glow curves using 2 °C/s heating rate were obtained. The samples were readout immediately after irradiation. The glow curves obtained by fading at the end of one day (24 h) were considered in order to analyze their structure. Figure 5. (a) shows the experimental glow curve deconvolved by four glow peaks. The activation energy (E) values (0.59 – 1.16 eV) increased as the maximum temperature (T_m) increases (195–462°C) (Table 1). While the first peak (195 °C) was fast decay their TL intensity and shifted to 188 °C in the glow curve after one day (Figure 5.b), and slightly diminish for the second and fourth peaks at 270 and 466 °C, respectively, was observed (Table 1). The main glow peak at 333 °C practically remains at the same temperature (334 °C) after one day of fading. Finally, T_m shows variation about 1 to 7 °C that may be ascribed to the retrapping charges in the distribution levels. This fading effect on the structure of the glow curve seems reflects in the kinetic order (b) values which were close to the second order. It was observed that the main glow peak, experimental and deconvolved, was located at about 333 °C and in consequences it can be considered as a good prospect for dosimetric peak if the synthesis of this magnesium borate is carried out by solution-assisted method. The TL phenomenon in this case, were well described by the general

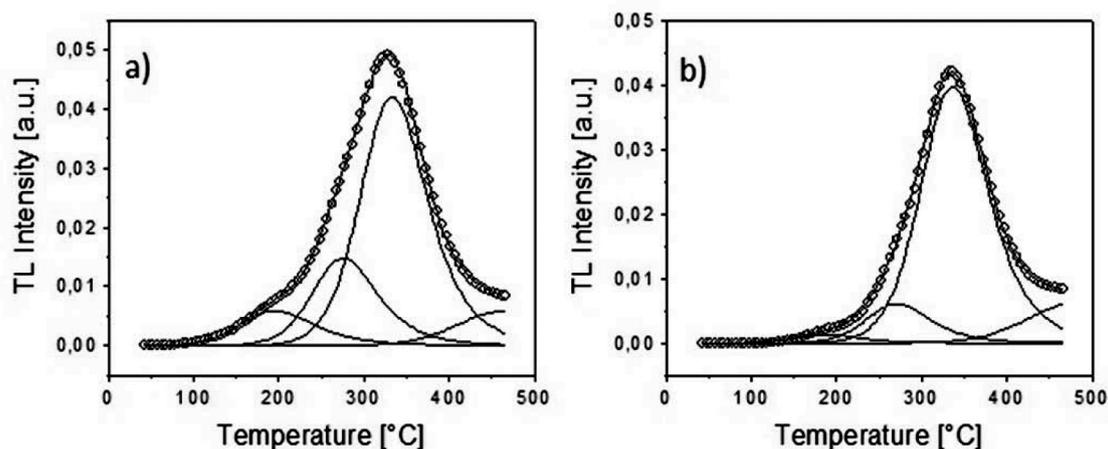


Figure 5. Experimental glow curve (open circles) deconvolved with four TL glow peaks (thin solid lines) assuming the GOK model. The thick solid line is the sum of the TL glow peaks; a) complex glow curve obtained at 1 Gy, b) glow curve after fading at the end of one day.

order kinetics (GOK) model, because the Figure of Merit (FOM) for the glow curves was less than 1.2 %.

Table 1. Kinetics parameters of the glow peaks deconvolved by using the GOK model.

	T_m [°C]	E [eV]	s [s ⁻¹]	b	FOM
TL Glow Curve					1.1%
Peak 1	195	0.59	1.23×10^{11}	2.1	
Peak 2	275	0.95	9.09×10^{10}	2.1	
Peak 3	333	1.12	1.07×10^{12}	2.0	
Peak 4	462	1.16	1.86×10^{11}	2.1	
1 day					1.2%
Peak 1	188	0.70	2.07×10^{12}	2.1	
Peak 2	270	0.96	2.99×10^{11}	2.1	
Peak 3	334	1.12	1.06×10^{12}	2.0	
Peak 4	466	1.15	1.04×10^{11}	2.1	

4. Conclusions

Dysprosium doped MgB_4O_7 and un-doped crystalline phosphor were synthesized using the solution-assisted method. The formation of the crystalline matrix was determined by means of X-ray diffraction. The highest thermoluminescent sensitivity was obtained with annealing at 450°C. The TL intensity of magnesium tetraborate was improved with 4 mol% of Dy^{3+} dopant. The introduction of Dy^{3+} with varying concentrations in the matrix strong activates the TL phenomenon and changed the structure of the glow curves of the MgB_4O_7 . It seems that the experimental TL glow curves was forming by three overlapped peaks at

about 124, 195 and about 336 °C. The complex glow curves were acceptable deconvolved by four peaks, with FOM less than 1.2%, indicating that the general order kinetics model was appropriate to well described the thermoluminescence of this phosphor. $MgB_4O_7:Dy^{3+}$ compound presents an interesting and useful linear dose-response for measuring low β -radiation doses, which can be useful in radiation therapy doses.

Acknowledgements

This work has been partly funded by DGAPA-UNAM through the IN112617 project. The first author (Osiel Legorreta Alba) acknowledge support from Programa de Maestría y Doctorado en Ciencias Químicas UNAM and thanks CONACYT for the scholarship number 604038.

References

- [1] O. Annalakshmi, M. T. Jose, U. Madhusoodanan, J. Sri devi, B. Venkatraman, G. Amarendra, A. B. Mandal, *Radiat. Eff. Defects Solids*, **169**(7), 636–645 (2014). <https://doi.org/10.1080/10420150.2014.918128>
- [2] A. J. J. Bos, *Nucl. Instrum. Methods B*, **184**, 3–28 (2001). [https://doi.org/10.1016/S0168-583X\(01\)00717-0](https://doi.org/10.1016/S0168-583X(01)00717-0)
- [3] L. L. Campos, O. O.Fernandes, *Radiat. Prot. Dosim.*, **33**(1/4), 111–113 (1990). <https://doi.org/10.1093/oxfordjournals.rpd.a080769>
- [4] G. Cedillo Del Rosario, E. Cruz-Zaragoza, M. García Hipólito, J. Marcazzó J. M. A. Hernández, H. S. Murrieta, *Applied Radiation and Isotopes*, **127**, 103–108 (2017). <https://doi.org/10.1016/j.apradiso.2017.05.018>

- [5] E. Cruz-Zaragoza, G. Cedillo Del Rosario, M. García Hipólito, J. Marcazzó, J. M. A. Hernández, E. Camarillo, H. S. Murrieta, *J. Nucl. Phys. Mat. Sci. Rad. App.*, **5(1)**, 169–178 (2017).
<https://doi.org/10.15415/jnp.2017.51016>
- [6] E. Cruz-Zaragoza, C. Furetta, J. Marcazzó, M. Santiago, C. Guarneros, M. Pacio, R. Palomino, *J. Lumin.*, **179**, 260–264 (2016).
<https://doi.org/10.1016/j.jlumin.2016.07.003>
- [7] T. Depci, G. Ozbayoglu, A. Yilmaz, *Metall. Mater. Trans. A*, **41(10)**, 2284–2594 (2010).
<https://doi.org/10.1007/s11661-010-0341-0>
- [8] M. Dogan, A. N. Yazici, *Journal of Optoelectronics and Advanced Materials*, **11(11)**, 1783–1787 (2009).
- [9] C. M. H. Driscoll, S. J. Mundy, J. M. Elliot, *Radiat. Prot. Dosim.*, **1(2)**, 135–137 (1981).
- [10] D. Evis, A. Yucel, N. Kizilkaya, *et al.*, *Applied Radiation and Isotopes*, **116**, 138–142 (2016).
<https://doi.org/10.1016/j.apradiso.2016.08.004>
- [11] F. Fukuda, N. Takeuchi, *J. Mater. Sci. Lett.*, **8**, 1001–1002 (1989).
<https://doi.org/10.1007/BF01730467>
- [12] C. Furetta, *Handbook of Thermoluminescence*. Singapore: World Scientific Publishing Co. Pte. Ltd. (2003).
<https://doi.org/10.1142/5167>
- [13] C. Furetta, G. Kitis, P. S. Weng, T. S. Chu, *Nucl. Instrum. Methods A*, **420**, 441–445 (1999).
[https://doi.org/10.1016/S0168-9002\(98\)01198-X](https://doi.org/10.1016/S0168-9002(98)01198-X)
- [14] T. Hitomi, *Radiothermoluminescence Dosimeter and Materials*. U.S. Patent Filed no. 213 950 (1971).
- [15] M. Israeli, N. Kristianpoller, R. Chen, *Phys. Rev. B*, **6(12)**, 4861–4867 (1972).
<https://doi.org/10.1103/PhysRevB.6.4861>
- [16] S. P. Lochab, A. Pandey, P. D. Sahare, R. S. Chauhan, N. Salah, R. Ranjan, *Phys. Status Solidi A*, **204(7)**, 2416–2425 (2007).
<https://doi.org/10.1002/pssa.200622487>
- [17] C. F. May, J. A. Partridge, *J. Chem. Phys.*, **40**, 1401–1409 (1964).
<https://doi.org/10.1063/1.1725324>
- [18] E. F. Mische, S. W. S. McKeever, *Radiat. Prot. Dosim.*, **29(3)**, 159–175 (1989).
<https://doi.org/10.1093/oxfordjournals.rpd.a080548>
- [19] M. Prokic, *Nucl. Instrum. Methods*, 175, 83–86 (1980).
[https://doi.org/10.1016/0029-554X\(80\)90262-1](https://doi.org/10.1016/0029-554X(80)90262-1)
- [20] P. D. Sahare, M. Singh, P. Kumar, *J. Lumin.*, **160**, 158–164 (2015).
<https://doi.org/10.1016/j.jlumin.2014.11.042>
- [21] M. Santiago, C. Grseli, E. Caseli, M. Lester, A. Lavat, F. Spano, *Phys. Stat. Sol. (a)*, **185(2)**, 285–289 (2001).
[https://doi.org/10.1002/1521-396X\(200106\)185:2<285::AID-PSSA285>3.0.CO;2-9](https://doi.org/10.1002/1521-396X(200106)185:2<285::AID-PSSA285>3.0.CO;2-9)
- [22] L. F. Souza, P. L. Antonio, L. V. E. Caldas, D. N. Souza, *Nucl. Instrum. Methods Phys. Res. A*, **784**, 9–13 (2015).
<https://doi.org/10.1016/j.nima.2014.12.030>
- [23] A. K. Subanakov, Zh. G. Bazarova, A. I. Nepomnyschih, A. V. Perevalov and B. G. Bazarov, *Inorg. Mater.*, **50(5)**, 485–488 (2014).
<https://doi.org/10.1134/S0020168514050185>
- [24] J. H. Schulman, R. D. Kirk, E. J. West, *In Proc. Int. Conf. on Luminescence Dosimetry*, US AEC Symposium series CONF-650637 (pp. 113–117). Stanford University, USA (1967).
- [25] D. I. Shahare, S. J. Dhoble, S. V. Moharil, *J. Mater. Sci. Lett.*, **12**, 1873–1874 (1993).
<https://doi.org/10.1007/BF00540016>
- [26] M. Takenaga, O. Yamamoto, T. Yamashita, *Nucl. Instrum. Methods*, **175**, 77–78 (1980).
[https://doi.org/10.1016/0029-554X\(80\)90259-1](https://doi.org/10.1016/0029-554X(80)90259-1)
- [27] E. G. Yukihara, E. D. Milliken, B. A. Doull, *J. Lumin.*, **154**, 251–259 (2014).
<https://doi.org/10.1016/j.jlumin.2014.04.038>