Functional Materials 13, No.1 (2006)

Kinetic parameters of charge carrier traps in magnesium-aluminum spinel crystals after X-ray and UV irradiation

V.A.Kobyakov, V.N.Volokitin, D.N.Shevtsova, L.A.Lytvynov*

V.Karazin Kharkiv National University,
4 Svobody Sq., 61077 Kharkiv, Ukraine
*Institute for Single Crystals, STC "Institute for Single Crystals"
National Academy of Sciences of Ukraine,
60 Lenin Ave., 61001 Kharkiv, Ukraine

Received July 6, 2005

Thermoluminescence (TL) of non-stoichiometric $MgO{\cdot}2.5Al_2O_3$ spinel single crystals in the green emission range after X-ray and UV irradiation has been studied. The TL maximum at 420 K emitted within that spectral region at linear heating has been found to be a complex one in spectral composition and in temperature. Using the self-consistent heating, the temperature positions of TL maxima caused by release of charge carriers from a set of traps at various activation energies. The recombination luminescence observed has been shown to occur only according to the second order kinetics. The occupation efficiency of shallow traps of charge carriers is found to increase after UV irradiation. The activation energy values and effective frequency factors have been determined for some traps.

Исследована термолюминесценция (ТЛ) монокристаллов нестехиометрической шпинели $MgO{\cdot}2.5Al_2O_3$ в зеленой области свечения после УФ и рентгеновского облучения. Определено, что наблюдаемый при линейном нагреве максимум ТЛ при температуре 420 К, высвечиваемый в этой области спектра, является сложным как по спектральному составу, так и по температуре. С помощью метода самосогласованного нагрева удалось определить положения максимумов ТЛ, обусловленных высвобождением носителей заряда из набора ловушек с разной энергией активации. Показано, что наблюдаемое рекомбинационное свечение проходит только по второму порядку кинетики. Установлено, что эффективность заполнения мелких ловушек носителей заряда выше при УФ облучении. Для некоторых ловушек носителей заряда определены значения энергии активации и эффективные частотные факторы.

The magnesium-aluminum spinel is a complex oxide with cubic lattice of *Fd3m* symmetry. The unit cell contain 32 oxygen atoms forming a close packing. In the spinel structure, cations occupy 16 octahedral sites of 32 ones and 8 tetrahedral sites of 64 ones. The natural spinel ($MgAl_2O_4$) is a normal one, i.e., the Mg^{2+} ions occupy the tetrahedral positions and Al^{3+} ions, the octahedral ones. The spinel crystals grown in laboratory are inverted in part, that is, a certain number of Mg^{2+} ions occupies octahedral positions while the same number of Al^{3+} ions, tetrahedral ones, thus forming so-called anti-site defects. The inversion parameter that characterizes the number of anti-site defects amounts 0.15 to 0.27 for stoichiometric crystals [1].

Besides of stoichiometric $MgAl_2O_4$ crystals, the spinel structure is formed when the aluminum oxide content is increased up to 7.3 molar parts, i.e., in $MgO{\cdot}nAl_2O_3$ where $1 \le n \le 7.3$. The addition of Al_2O_3 results in occupation of the tetrahedral sites

by Al^{3+} ions and an additional number of unoccupied octahedral sites appears [2]:

$$(1 - y)MgAl_2O_4 + y^{Al}\square_{3}O_4 \rightarrow$$
$$\rightarrow (Mg_{1-y}Al_y)^{IV}(Al_{2-y/3}\square_{y/3})^{VI}O_4,$$

where $y = (n - 1)/(n + 3/8)$ is the nominal inversion extent due to the stoichiometry deviation; $\square$, a cationic vacancy. The inversion extent of non-stoichiometric crystals at $n \leq 3.0$ amounts 0.35 to 0.43 [3].

Irradiation of the spinel crystals with X-rays or UV light results in recharging of the defects as well as in capturing of charge carriers in traps. The carrier release from the traps followed by recombination at the emission centers causes luminescence in UV, green, and red spectral regions [4]. The green emission is believed to be associated with processes involving manganese ions present in the crystals as a non-controlled impurity [5]. This emission is observed in X-ray luminescence (XRL) spectra, under vacuum UV excitation, as well as in thermoluminescence (TL) after irradiation with γ quanta, X-rays, or UV light. It is just TL that is the most sensitive to the recombination processes.

TL in stoichiometric spinel crystals under linear heating was studied in several works [6, 7] where the thermal glow (TE) curves were shown to have a complex character and to consist of two or more main peaks. The overlapping of experimental peaks is such that attempts to separate them using a partial annealing results only in a shift of the resulting peak towards higher temperatures [8]. The self-consistent heating method used by us to study the TL of stoichiometric spinel crystals made it possible to reveal the complex character of glow peaks as well as to determine the activation energy and frequency factors for traps in stoichiometric crystals [9].

TL of non-stoichiometric crystals has been not studied essentially. The crystal stoichiometry variations result in changed lattice parameter and in formation of additional cationic vacancies. This should cause changes in the capturing center parameters and spatial redistribution thereof. The TL of non-stoichiometric crystals after UV irradiation includes also peaks in violet, green, and red spectral regions; the peaks, however, are shifted towards lower temperatures as compared to stoichiometric crystals [10, 11]. In this work, the kinetic characteristics have been measured for TL processes caused by the presence of manganese ions in $MgO{\cdot}2.5Al_2O_3$ crystals having the emission maximum near 518 nm.

It is rather difficult to obtain the kinetic characteristics of charge carrier traps (activation energy, kinetic order, frequency factor) proceeding from glow curves, since there is no finite analytical solution for a TE curve at linear heating. The methods for determining the trap parameters based on consideration of the glow curve shape and position assume as a rule some approximations that may result in significant errors and are applicable to elementary isolated peaks only. Another approach consists in mathematical fitting of the glow curve shape by varying the kinetic characteristics. A high-precision fitting can provide the light sum under the curve but does not imply any physical model of the thermal glow process, since the phenomenological characteristics, although defining uniquely the glow curve, are not characterized unambiguously thereby. When one trap class are emptied, the kinetics becomes often more complicated, including transition from a 1st order process to a 2nd order one, or vice versa. In such cases, the analysis of the glow curve shape does not provide the selection of the process kinetic order and the calculation of main parameters.

In this connection, to find a means for quantitative determination of phenomenological characteristics seems to be of importance. Those characteristics can be obtained using a modified TL method, so-called the self-consisted heating [12, 13]. The experiment consists in realization of the sample heating in such a manner that the luminescence intensity remains at a constant level (the constant signal method). The method is described in detail in [9].

To interpret the results obtained, let the basic relations be considered. Proceeding from equations describing the glow intensity as a function of temperature, $J(T)$, the differentiation and appropriate substitutions give the expressions for temperature dependence of heating rate, $\beta(T)$, providing a constant intensity value J in the case of the 1st order kinetics

$$\beta(T) = \frac{kT^2\omega}{E}\exp\left(-\frac{E}{kT}\right), \quad (1)$$

while for the 2nd order kinetics,

$$\beta(T) = \frac{2kT^2\omega}{E}\exp\left(-\frac{E}{2kT_0} - \frac{E}{2kT}\right), \quad (2)$$

where T is instantaneous absolute temperature at heating; T_0, the initial temperature from which the self-consisted heating starts; ω, the frequency factor; E, the activation energy of the charge carrier release

from the traps; k, the Boltzmann constant. It is convenient to present the Eqs.(1) and (2) as follows:

in the case of the 1st order kinetics

$$\ln\frac{\beta(T)}{kT^2} = -\ln E + \ln\omega - \frac{E}{kT}, \qquad (3)$$

while for the 2nd order kinetics,

$$\ln\frac{\beta(T)}{kT^2} = -\ln\frac{E}{2} + \ln\omega - \frac{E}{2kT_0} - \frac{E}{2kT}. \qquad (4)$$

It follows from (3) and (4) that the temperature dependence of heating rate providing the constant signal level is linear in the $\ln(\beta/kT^2) = f(1/kT)$ coordinates. The corresponding straight line slope defines the activation energy E in the case of the 1st order kinetics or $E/2$ for the 2nd order kinetics. Continuing that line to crossing point with the ordinate axis, it is possible to determine the effective frequency factor. If a transition from the 1st order to the 2nd one or vice versa occurs during the TL, the plot will contain two linear sections corresponding to one and the same peak. For various J_i values, the linear sections corresponding to the 2nd order kinetics should be shifted while those answering to the 1st one should fall on one and the same straight line. In this case, any ambiguity in determination of activation energy, effective frequency factor, and the relaxation kinetics order is eliminated, since at the 1st order kinetics, the heating regime providing the constant signal level is independent of the J_i value, in contrast, it depends thereon at the 2nd kinetic order.

The constant signal method (self-consistent heating) was realized using a setup described before [9]. The setup is based on a MSD-2 monochromator with 4.6 nm/mm resolution and is controlled by a PC that provides the TL spectra and glow curves measurements at linear heating as well as the self-consistent heating realization. All the regimes are realized using programs controlling the monochromator, heater, as well as measurements in the selected mode and recording the results. The TL spectra and glow curves were measured at the sample heating rate of 0.2 K/s in the following spectral regions: for review spectra, 200 to 800 nm, for detailed studies, 460 to 600 nm. The monochromator passing time was about 10 s for detailed spectral ranges, and about 17 s for the review one. When measuring TL and glow curves, the temperature change was linear to within 0.2 %. In the self-consistent heating mode,

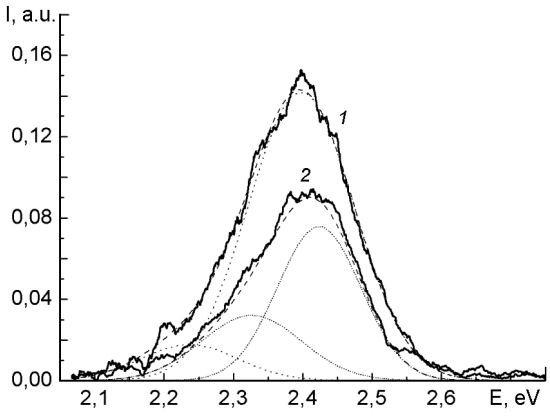

Fig. 1. TL spectrum of a $MgO{\cdot}2.5Al_2O_3$ crystal in glow peakm (420 K) after UV (*1*) and X-ray (*2*) irradiation measured at constant heating rate.

the sample emission intensity was maintained at the preset constant level to within 2 to 3 % (under account for noise). The temperature was controlled by a Chromel/Alumel thermocouple. To study the TL, samples of $7\times8\times0.5$ mm^3 were cut out of a $MgO{\cdot}2.5Al_2O_3$ single crystal. The samples were irradiated with X-rays using an URS-55M unit at the voltage on the BSV-2Cu tube of 40 kV and the tube current of 10 mA, the sample distance from the tube output window being 2.5 cm. A water-cooled LD(D) deuterium lamp of 400 W power was used as the UV light source, the sample-to-lamp distance being also 2.5 cm. The sample was cooled with air flow. The irradiation duration at the glow curve measurements and at self-consistent heating was 0.5 h with both radiation sources.

After X-ray and UV irradiation of nonstoichiometric crystals, a TL maximum in green region is observed at 420 K. It is ascribed to recombination luminescence involving Mn^{2+} ions that enter the spinel crystal lattice mainly into tetrahedral positions [5]. The peak is a complex one. The expansion into Gaussians using PC reveals two emission bands differing in maximum positions and intensity ratios depending on the irradiation type (Fig. 1). The main emission band maximum determined using the expansion correspond to the photon energy of 2.4 eV after UV irradiation and 2.42 eV after X-ray one. Besides, there are weak bands with 2.23 and 2.33 eV energy, respectively. After UV irradiation, the 2.23 eV band contributes to the main TL emission insignificantly. After X-ray irra-

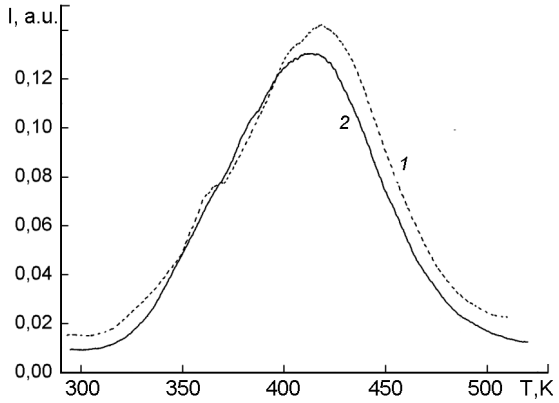

Fig. 2. Glow curves of a $MgO{\cdot}2.5Al_2O_3$ crystal at 517 nm wavelength after 30 min UV (*1*) and X-ray (*2*) irradiation measured at constant heating rate.

diation, the band overlap and intensity ratio is such that the 2.33 eV band contribution can be revealed by measurements. Since the main TL bands are rather wide, the glow curve measurements and the self-consistent heating after UV and X-ray irradiation were carried out at 517 nm (2.4 eV) wavelength, the registered spectrum width being 6 nm. The measured glow curves at linear heating (at 517 nm) are shown in Fig. 2. From those curves, the constant signal intensity at $J_1 = 0.1J_{max}$, $J_2 = 0.2J_{max}$, and $J_3 = 0.3J_{max}$ were determined.

To determined the kinetic parameters from the results measured using the self-consistent heating, the plots presented in Figs. 3 and 4 were constructed. The dependence is rather complex; nevertheless, the curves are shifted at different values of initial level, independent of the curve type. Proceeding from the physical principles of the method, linear sections can be distinguished. Moreover, none of those sections falls on the same line. This evidences that the recombination processes at TL after both UV and X-ray irradiation run according to the 2nd kinetic order only. The same kinetic order was observed when the green region TL of the stoichiometric spinel crystals was studied [8]. The initial signal levels were preset under assumption that there is only one glow peak or at least the intensity of the 420 nm maximum is the defining one (Fig. 2). The dependences obtained in experiment and shown in Figs. 3 and 4 evidence, however, a rather complex structure of glow curve that requires a more detailed analysis.

The linear sections corresponding to physical principles of the method are observed only at temperatures exceeding 400 K after both

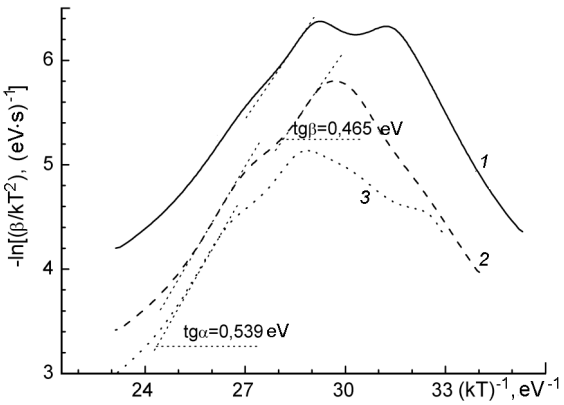

Fig. 3. $\ln(\beta/kT^2) = f(1/kT)$ plots obtained using the constant signal method after UV irradiation of a $MgO{\cdot}2.5Al_2O_3$ crystal. Signal intensity: $0.1J_{max}$ (*1*), $0.2J_{max}$ (*2*), $0.3J_{max}$ (*3*).

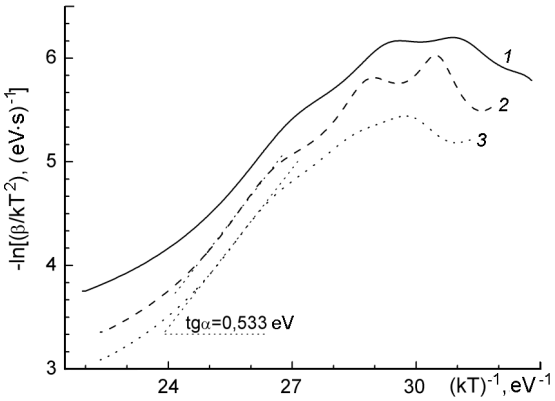

Fig. 4. $\ln(\beta/kT^2) = f(1/kT)$ plots obtained using the constant signal method after X-ray irradiation of a $MgO{\cdot}2.5Al_2O_3$ crystal. Signal intensity: $0.1J_{max}$ (*1*), $0.2J_{max}$ (*2*), $0.3J_{max}$ (*3*).

UV and X-ray irradiation. Since the process runs according to the 2nd kinetic order only, the transition from one linear section to other one answers to transition from one emission maximum to another. The positions of those maxima should correspond approximately to the middle of the corresponding linear section. Thus, it is possible to estimate approximately the positions of two maxima. After UV irradiation, those are positioned at 446±10 K and 380±10 K while after X-ray one, at 456±10 K and 410±10 K. The determination of the 410 K maximum is affected, as mentioned above, by the high overlap extent of the emission band with the 2.32 eV maximum having the highest intensity at that temperature (Fig. 1).

Let us suppose that the glow peak includes a maximum with lower emission temperature and lower intensity and that the

preset signal levels for the self-consistent heating correspond to the highest intensity. In this case, to provide the constant signal intensity, the heating rate should decrease as the low-temperature maximum is emitted, because the charge carrier release from traps with lower activation energy makes an additional contribution to the recombination emission intensity. The heating rate decrease will cause negatively sloped sections in the $\ln(\beta/kT^2) = f(1/kT)$ plots. In the competing emission process, the negative slope will be kept up to the end of the low-temperature maximum emission. Therefore, it can be believed that the run of dependence observed after UV irradiation (Fig. 3) at temperatures lower than 400 K evidences the presence of maxima in that temperature region. Judging from of middle point positions of the negative slope sections, the low-temperature maxima can be estimated to correspond to 380±10 K and 350±10 K.

After X-ray irradiation, the shallow trap occupation efficiency is lower that after UV one (Fig. 2), and the intensity ratio is most likely different. However, from Fig. 4, the maxima at 380±10 K and 350±10 K can be supposed. The possible presence of those maxima is evidenced also by the glow curve runs (Fig. 2). Thus, basing on the results obtained using the self-consistent heating, it could be stated that the glow curve measured at 517 nm wavelength contains maxima at 350±10 K, 380±10 K, 450±10 K and 400±10 K. A set of charge carrier traps with different activation energy values corresponds to those maxima.

In the course of measurements using the self-consistent heating method, the low-temperature maxima contribute to intensity of the preset initial level. Therefore, the linear section lengths depend on the overlap extent, intensity ratio and width of the TE peaks. It is seen from Figs. 3 and 4 that the linear sections making it possible to determine the activation energy are present for the high-temperature maxima only. The activation energy determined from the slope of linear sections after UV irradiation for carriers released from the traps and involved in recombination processes near 450 K is 1.08±0.01 eV. Near 400 K, it amounts 0.93±0.01 eV. We failed to determine the activation energy for the 2nd high-temperature maximum after X-ray irradiation because of the presence of the 2.33 eV maximum in the TL spectrum.

The effective frequency factor for the traps with 1.08±0.01 eV activation energy after UV and X-ray irradiation amounts (4 to 7)·10^{12} s^{-1}. As to traps with 0.93±0.01 eV activation energy, it is (3 to 5)·10^{11} s^{-1}.

Thus, the studies of green spectral region TL in $MgO{\cdot}2.5Al_2O_3$ spinel single crystals after X-rayglowTE peak obtained under linear heating is a complex one. It contains two emission bands and the TL is due to the charge carrier release from the traps having different activation energies. Using the constant signal method, the values of TE peaks for various trap types have been estimated. The release of charge carriers from traps responsible for the recombination luminescence in green spectral region runs according to the 2nd order kinetics only. The activation energy values for traps of the same type are independent of the irradiation type. The occupation efficiency of shallow traps is higher under UV irradiation than under X-ray one.

The work has been carried out under financial support by Civil Research and Development Foundation (USA) for independent states of former USSR (CRDF), Grant No.UE2-2226; by Science and Technology Center in Ukraine (STCU), Grant No.2058; and by Ministry of Education and Science of Ukraine, Project No.7-13-03.

References

1. K.E.Sickafus, J.M.Wills, N.W.Grimes et al., *J. Am. Ceram. Soc.*, **82**, 79 (1999).
2. G.Patrat, M.Brunel, F. de Bergevin, *Acta Cryst.*, **A36**, 47 (1980).
3. R.Basso, S.Cabonin, A.D.Giusta, *Z. Krist.*, **194**, 111 (1991).
4. Yu.G.Kazarinov, V.T.Gritsyna, V.A.Kobyakov et al., *VANT, Ser. Fiz. Rad. Povr.*, **3(81)**, 53 (2002).
5. O.N.Boksha, T.M.Varian, A.A.Popova, *Kristallografiya*, **17**, 1063 (1972).
6. A.Ibarra, D.F.Mariani, M.Jimenez de Castio, *Phys. Rev.*, **44**, 12158 (1991).
7. T.K.Kim, H.S.Shoe, J.I.Lee, C.N.Wang, *J. Korean Phys. Soc.*, **30**, 347 (1997).
8. G.S.White, R.V.Jones, J.H.Crawford et al., *J. Appl. Phys.*, **53**, 265 (1982).
9. V.A.Kobyakov, V.T.Gritsyna, Yu.G.Kazarinov, V.N.Volokitin, *VANT. Ser. Fiz. Rad. Povr.*, **4(87)**, 36 (2005).
10. T.I.Voytsenya, V.T.Gritsyna, V.B.Kolner et al., *Izv. AN SSSR, Ser. Neorg. Mater.*, **16**, 1580 (1980).
11. V.T.Gritsyna, T.I.Voytsenya, T.I.Korneeva et al., *Zh. Tekhn. Fiz.*, **50**, 2220 (1980).
12. A.A.Gailitis, P.A.Kulis, in: Proc. of Latv. Univ., **208**, 66 (1974) [in Rusisan].
13. A.A.Gailitis, Ya.L.Yansons, I.K.Vitol, *Izv. AN SSSR, Ser. Fiz.*, **33**, 977 (1969).

Кінетичні параметри пасток носіїв заряду в кристалах магнійалюмінієвої шпінелі після рентгенівського та УФ опромінення

В.А.Кобяков, В.Н.Волокітін, Д.М.Шевцова, Л.А.Литвинов

Досліджено термолюмінесценцію (ТЛ) монокристалів нестехіометричної шпінелі $MgO \cdot 2.5Al_2O_3$ у зеленій області випромінювання після УФ та рентгенівського опромінення. Визначено, що максимум ТЛ, який спостерігається при лінійному нагріванні при температурі 420 К, і випромінює у визначеній області спектра, є складний як за спектральним складом, так і за температурою. За допомогою методу самоузгодженого нагріву вдалось визначити положення максимумів ТЛ, які обумовлені звільненням носіїв заряду із набору пасток з різною енергією активації. Показано, що рекомбінаційне випромінювання, що спостерігається, відбувається виключно за другим порядком кінетики. Встановлено, що ефективність заповнення мілких пасток носіїв заряду вища при УФ опроміненні. Для деяких пасток носіїв заряду визначено значення енергії активації та ефективні частотні фактори.