O. STANOVYI,[1] S. KUTOVYY,[1] YU. MOROZOV,[1] A. NAUMENKO,[1] I. DMITRUK,[1]
A. BORODYANSKA [2]

[1] Taras Shevchenko National University of Kyiv
(64/13, Volodymyrs'ka, Kyiv 01601, Ukraine)
[2] Frantsevich Institute for Problems of Materials Science, Nat. Acad. of Sci. of Ukraine
(3, Krzhizhanovs'kyi Str., Kyiv 03680, Ukraine)

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LOW-TEMPERATURE THERMOLUMINESCENCE STUDIES OF THE NANOCRYSTALLINE YTTRIA-STABILIZED ZIRCONIA

The spectra of thermoluminescence (TL) of nano-sized powders ZrO_2 stabilized by Y_2O_3 (YSZ) in the temperature range of 80–350 K have been studied for the first time. For comparison, the TL spectra of pure ZrO_2 are obtained. It is found that the TL in undoped ZrO_2 is mainly caused by intrinsic defects, whereas, in doped zirconia, it is caused by dopants. Using the fractional curve glowing method, the values of activation energies of traps in YSZ have been determined. The model of TL in YSZ has been proposed.

Keywords: thermoluminescence, zirconia, method of fractional curves, activation energies of traps.

1. Introduction

$ZrO_{2(1-x)}Y_2O_{3(x)}$ crystals are zirconium oxide (zirconia) stabilized by ittria (YSZ) in the tetragonal or cubic phase. YSZ crystals have numerous successful applications; for example, they can be used as ion conductors in fuel cells or oxygen sensors due to their relatively high ion conductivity [1, 2].

The studies of nanocrystalline YSZ with the aim to find more optimal technologies of the material synthesis [3, 4] and to improve its characteristics remain promising. The application of this material in optics is less perspective due to technological difficulties in the fabrication of optically pure single crystals. Therefore, the optical properties of YSZ, particularly, the energy characteristics of defects, are studied insufficiently.

It was reported that the ionic conductivity of YSZ can be enhanced by radiation [5], which leads to changes in the defect structure of a crystal. The broad absorption bands of YSZ in the visible and ultraviolet regions appeared after the irradiation with ions or X-rays [6, 7]. The EPR studies provide a possibility to associate the absorption bands with two kinds of defects – electron traps: centers of F^+-type (including once ionized vacancies of oxygen) and T-centers (Zr^{3+} (Y^{3+}) in the position between two vacancies of oxygen in the center of a trigonal distorted area) [8]. It was noted also the presence of hole traps (O^--centers), the EPR signal from which was an order of magnitude lower, but it increased significantly after the ultraviolet irradiation [9].

Many papers reported a decrease in the intensity of some EPR lines under the heating of samples irradiated with X-rays or ions at low temperatures. In [7], the partial weakening of the EPR signal associated with T-centers and the almost complete disappearance of O^--centers were found at 150 K. The authors of work [10] observed the thermal treatment (annealing) of paramagnetic centers (T- and F^+-type) at temperatures ≈ 500 K and the related thermoluminescence with a wavelength of 620 nm. The estimated values of trap activation energies are within 0.7–1.4 eV. Previously, the observations of the weak TL near 100 K, which was associated with the hole traps, were reported.

The well-known method of thermostimulated luminescence (TL) is one of the indirect methods of study of point defects. This method is one of the most used ones for the investigation of energy characteristics of intrinsic and impurity point defects in alkali halides and many other crystals [11]. In our experiments, we found that the TL signal with sufficient intensity appears in the temperature interval, which is characteristic of the thermal purification of EPR centers (100–200 K). In this paper, we present the results of studies of the thermoluminescence of nanocrystalline YSZ with different percentages of Y_2O_3 and pure (undoped) ZrO_2.

2. Experimental Technique

ZrO_2 crystals have the monoclinic lattice at room temperature. It becomes tetragonal at the temperature above 1170 °C, and cubic above 2370 °C. The addition of Y_2O_3 stabilizes ZrO_2 in the tetragonal or cubic phase at room temperature [12]. Y_2O_3 added to ZrO_2 leads to the appearance of inclusions of the tetragonal phase. The crystal has the tetragonal lattice at a concentration of ittria more than 3 mol.% and the cubic symmetry at concentrations over 8 mol.%. We studied a series of samples with varying percentage of the stabilizing dopant: 0.66, 1.2, 3, and 8 mol.% of Y_2O_3 (certified samples, production of Tosoh Corp., Japan). The samples are the nanocrystalline powders with crystallite sizes of 7–14 nm. The powder was dispersed in ethanol and dried on a substrate to form a thin layer. The layer thickness was chosen to get a sufficient TL signal with minimal temperature gradient over the thickness of the sample.

The measurement of thermostimulated luminescence was carried out in the temperature range 80–350 K and at a heating rate of 0.2 K/s. The samples were placed in a vacuum cryostat and then excited by X-ray irradiation of a W BSV-2 tube operating at 30 kV, 10 mA through the beryllium window 0.5 mm in thickness at a temperature of 80 K. The excitation duration varied from 20 to 60 min. The integral intensity of TL was measured in the spectral region of sensitivity of a photomultiplier (300–800 nm).

3. Results and Discussion

3.1. Thermoluminescence

In Fig. 1, the experimental TL curves for YSZ samples with different percent amounts of ittria are presented; the plots are normalized on the intensity maximum.

The TL curves for YSZ samples with 0.66 mol.% Y_2O_3 (0.66-YSZ) and 1.2 mol.% Y_2O_3 (1.2-YSZ) almost coincide and have the same band at ≈ 110 K (for this reason, the curve of 1.2-YSZ is not presented in Figure, and the further study is focused on three samples – 0.66-YSZ, 3-YSZ and 8-YSZ). The only band 110 K in 0.66-YSZ and 1.2-YSZ has the high-temperature shoulder indicating the presence of at least one low-intensity component in it. In the TL curve of 3-YSZ, the most intense band has a maximum at 110 K too, but the components in the region 120–200 K are revealed more clearly. The TL curve of 8-YSZ differs considerably from those described above: the band with a maximum at 110 K is also observed, but it has a much larger FMHW. The high-temperature shoulder is more pronounced than for the samples with a lower concentration of ittria. Unfortunately, the analysis of the line shape doesn't allow us to determine the temperature position of the components.

To resolve the low-intensity bands and the band at 110 K, we used the "trimming" technique (heating up to different intermediate temperatures followed by the quenching to the excitation temperature) [13, 14], but it did not give the expected results: as the temperature of the "trimming" increases, the linear shift of the maximum was observed only instead of a decrease of the intensity at the stable maximum position. However, changes in the shape of the low-temperature wing were observed. This excludes the quadratic kinetics of luminescence, since, under the "trimming" procedure of a peak with quadratic kinetics, the shape of a peak is retained. In view of this fact, we assume that the band at 110 K consists of a large number of highly overlapped components, and the shallow traps are released firstly, the intensity of a low-temperature band shoulder decreases, the peak area also reduces, and the maximum of the total curve shifts to high temperatures.

The authors of work [15] reported about the TL-spectra of bulk YSZ, which consist of three wide separate bands with maxima at about 160, 280, and 425 K. In our spectra, the band 110 K corresponds to the band 160 K, but two others are not observed in our nanosamples. This can be caused by the non-radiative recombination of charge carriers on surface defects, which is negligible in bulk samples. This reason can determine the difference between nano- and bulk samples. Therefore it would be of interest to study the dependence of the TL-spectra on the size of crystallites. We plan to study this dependence in the future.

The TL curve of pure ZrO_2 differs significantly from that of YSZ. It consists of four intense bands at temperatures of 102, 131, 184, 258 K (see Fig. 2). The bands at 131 K and 184 K are complicated and consist of at least two components. There are also differences in FWHM for the TL peaks of undoped ZrO_2 and YSZ. The bands with maxima at 102 K and 131 K in pure ZrO_2 have FWHM equal to 14 K and 17 K, respectively, while the FWHM of the band at 110 K for YSZ is $\approx$ 35 K, which also favors the assumption of a large number of highly overlapped components.

The characteristic bands of a pure ZrO_2 are not observed in YSZ, so it is reasonable to consider that, in a doped zirconia, the emission is caused mainly by the defects created by the introduced dopant (yttria), while the traps in pure ZrO_2 should be governed by intrinsic defects. It has been observed that, after turning off the X-ray irradiation, the sample emits without heating and external excitation due to the release of carriers from shallow traps. The intensity of a low-temperature peak therewith decreases.

3.2. Decomposition of the TL bands into elementary components

Since the yttria concentration in some YSZ was 8 mol. percent, the interaction between defects occurs. As a result of this interaction, the local energy levels of traps form subzones. For a specific type of traps, the activation energy changes within the limits of a subzone. Further, at modeling the band shape and decomposing the TL curves into elementary components, we will proceed from this assumption.

We suppose that the density of energy states within a subzone can be approximately described by a Gauss function, and the equation modeling the TL peak is the convolution of the Randall–Wilkins equation [16–18] for the linear TL-kinetics with the Gauss function. The final equation for the approximation is:

$$I\,(T) = n_0 s \int\limits_0^\infty \exp\left(-\frac{E}{kT}\right) \exp\left[-\frac{1}{2}\left(\frac{E-E_0}{\Delta E}\right)\right] \times$$
$$\times \exp\left[-\frac{skT^2}{\beta E}\left(1-\frac{2kT}{E}\right)\exp\left(1-\frac{E}{kT}\right)\right] \mathrm{d}E,$$

where E_0 (eV) is the average value of activation energy of traps; ΔE (eV) is the energy width of a subzone; n_0 (m^{-3}) is the initial light-sum (which is proportional to the peak area); β (K/s) is the heating rate (specified in the experiment); s (s^{-1}) is the frequency factor; T (K) is the sample temperature; and k is the Boltzmann constant. The approximation parameters are: n_0, s, E_0, and ΔE.

The same equation can be written as a function of the parameters I_m, T_m, E_0, and ΔE, which are more convenient for analysis (I_m and T_m are the maximum intensity and temperature, respectively):

$$I\,(T) = I_m s \int\limits_0^\infty \exp\left[-\frac{1}{2}\left(\frac{E-E_0}{\Delta E}\right)\right] \times$$
$$\times \exp\left[1+\frac{E}{kT}\frac{T-T_m}{T_m}\right] \times$$
$$\times \exp\left[-\frac{T^2}{T_m^2}\left(1-\alpha_m\right)\exp\left(\frac{E}{kT}\frac{T-T_m}{T_m}\right)-\alpha_m\right]\mathrm{d}E,$$

where $\alpha_m = \frac{2kT_m}{E}$.

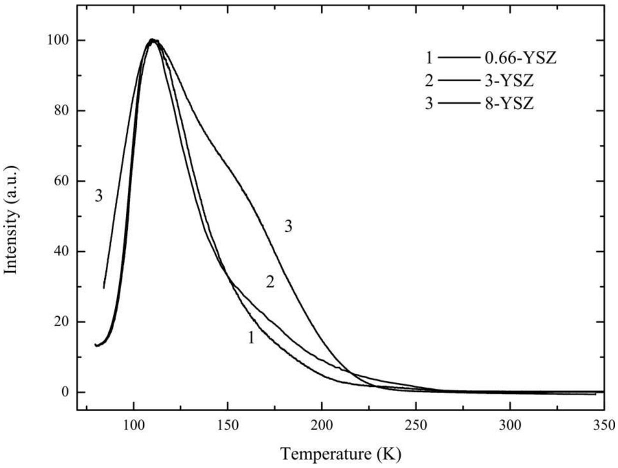


Fig. 1. TL-curves of stabilized ZrO_2 with a different percentage of Y_2O_3 (0.66, 3, and 8 mol.%)

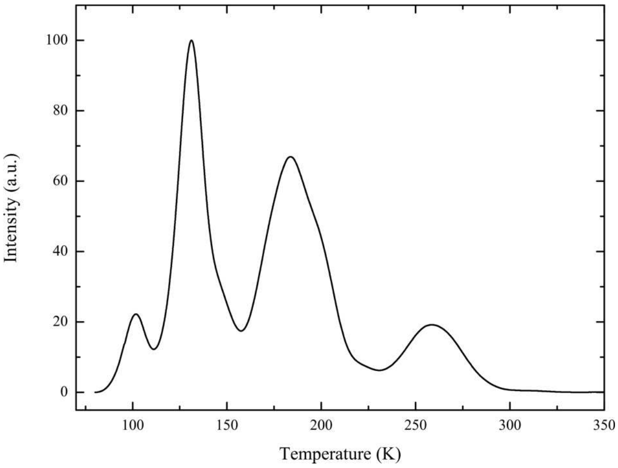


Fig. 2. TL-curve of undoped ZrO_2

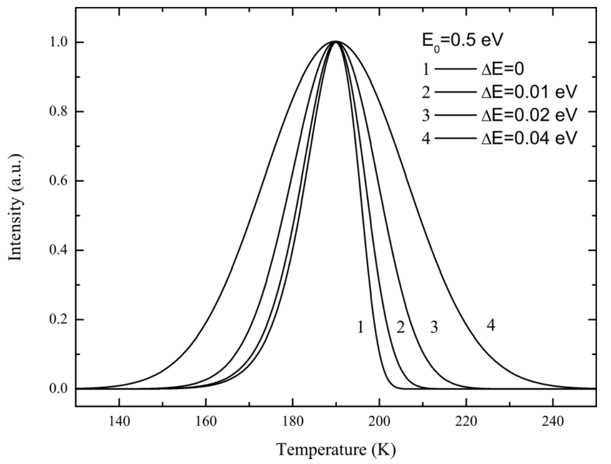
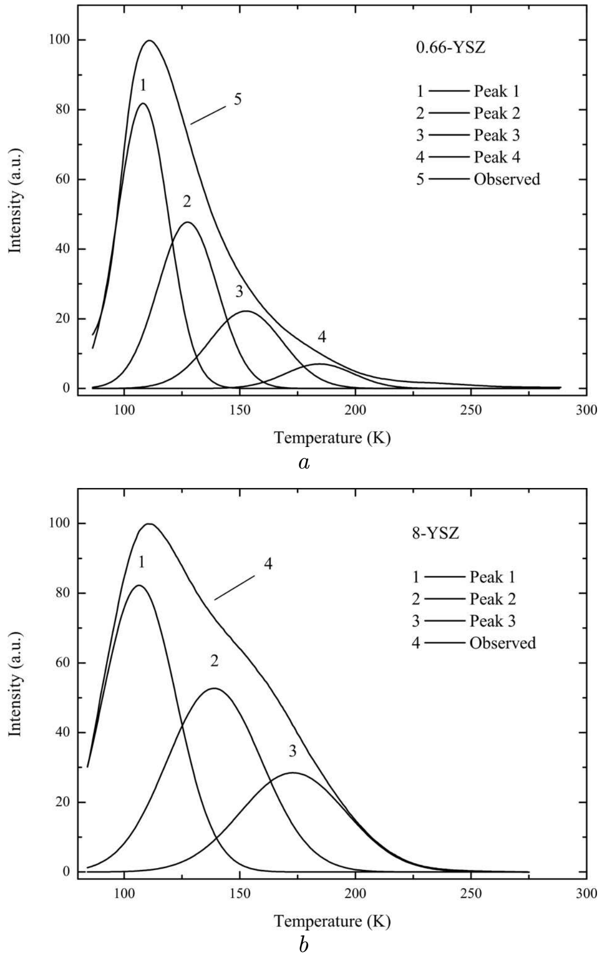


Fig. 3. Contours of the modeled TL peaks at different energy widths of a subzone ΔE



a

b

Fig. 4. Decomposition of the TL curve of 0.66-YSZ (*a*) and 8-YSZ (*b*) into elementary peaks

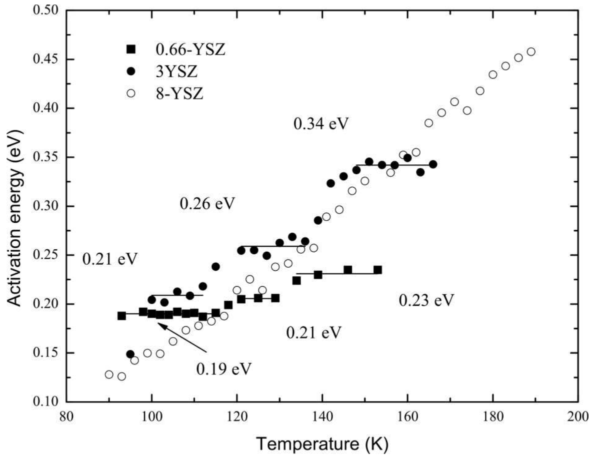


Fig. 5. Determination of the activation energy of traps for 0.66-YSZ, 3-YSZ, and 8-YSZ by the fractional curve method

In Fig. 3, the modeled TL peaks at different energy widths of a subzone ΔE are presented.

It should be noted that the dependence of the TL peak shape on four parameters makes it impossible, unfortunately, to assure the uniqueness of the decomposition; but the situation is improved by physical restrictions on approximation parameters; for some parameters, the initial values calculated from independent experiments were used.

Thus, the activation energy E_0 of traps was calculated with sufficient accuracy by the method of fractional curves (see the following section), and this parameter was varied within 10% relatively to its initial value. The method of fractional curves gives also opportunity to estimate the number and the temperature position of the peaks.

The decomposition of the TL curves of 0.66-YSZ and 8-YSZ into elementary peaks are shown in Fig. 4, *a*, *b*. The results of the decomposition for a collection of samples are presented in Table.

3.3. Calculation of the activation energies of traps

The analysis of changes of the intensity of the TL curves allowed us to obtain the energy position of traps. The trap energies were determined by the improved fractional curve glowing method (a version of the initial rise method). The experimental procedures and the method of data treatment were considered in detail in our previous works [19–21].

The calculated values of activation energy of traps for 0.66-YSZ, 3-YSZ and 8-YSZ are presented in Fig. 5. The dependences of the energy of traps on the temperature demonstrate, in general, a monotonic increase in the activation energy values; this is particularly due to the considerable overlapping of the TL peaks and the interaction between defects. For 8-YSZ, this concerns to a greater extent than for 0.66-YSZ, where the series of monoenergy values ("plateau") are observed. The activation energies of corresponding traps were determined as the average value of E on a "plateau". For 8-YSZ, the trap activation energy was estimated as the average of the calculated energies in the TL peak region.

3.4. The nature of TSL in YSZ

As was mentioned above, the X-ray irradiation of a sample produces electrons and holes which are localized at low temperatures (≈ 80 K) at corresponding centers. The electron traps are T and F^+-type (F^+, F^+_A, and F^+_{AA}), and the hole traps are O^--centers.

In [11], the thermoluminescence of YSZ at temperatures above 300 K and the annealing of paramagnetic electronic centers T and F^+ associated with it were observed. The depth of traps calculated in [11] was 0.7–1.4 eV. The TSL reported in present paper is associated with shallow traps with calculated depths of 0.1–0.45 eV. The electronic centers of F-type ($F^{++} + 2e^-$) or hole centers ($O^- + e^+$) can be these traps.

The computer calculations show that the ground state of F^+-type centers in YSZ lies 2.2 eV below the bottom of the conduction band [22]. For F-type centers, this value is 1.6 eV [22] or 2.1 eV [23]. In other words, the centers of the F and F^+-type form more deep traps, than those participating in the low-temperature TL observed by us in YSZ.

We propose the model, in which it is assumed that traps are O^- centers, and the recombination centers may be T or F^+ centers; the holes release from traps and recombine on the electronic centers. The role of hole centers in thermoactivated processes in YSZ is emphasized in [7, 8], where the authors reported the halving of the EPR signal of T-centers under the heating of a sample in the interval 100–200 K and the reduction of the EPR signal from O^- centers to almost zero.

Parameters of the modeled TL peaks at different energy widths of a subzone

Sample	Peak No.	T_m, K	E_0, eV	ΔE_0, eV	s, c^{-1}
0.66-YSZ	1	108	0.19	0.02	3×10^7
	2	128	0.2	0.02	4×10^6
	3	153	0.24	0.02	2×10^6
3-YSZ	1	107	0.21	0.02	5×10^8
	2	126	0.26	0.03	1×10^9
	3	158	0.33	0.03	2×10^9
8-YSZ	1	107	0.18	0.03	1×10^7
	2	139	0.29	0.04	1×10^9
	3	173	0.39	0.05	1×10^{10}

4. Conclusions

Thus, the thermoluminescence spectra of nano-sized powders ZrO_2 stabilized by Y_2O_3 have been studied in the temperature range 80–350 K for the first time.

It is established that the thermoluminescence in undoped ZrO_2 is mainly caused by intrinsic defects, whereas it is caused in doped zirconia by defects formed by the dopant (ittria).

Using the fractional curve glowing method, the values of the activation energies of traps in YSZ have been calculated.

The model of TL in YSZ has been proposed.

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О. Становий, С. Кутовий, Ю. Морозов,
А. Науменко, І. Дмитрук, Г. Бородянська

НИЗЬКОТЕМПЕРАТУРНА ТЕРМОЛЮМІНЕСЦЕНЦІЯ ОКСИДУ ЦИРКОНІЮ, СТАБІЛІЗОВАНОГО ІТРІЄМ

Резюме

Вперше досліджено спектри термостимульованої люмінесценції нанорозмірних порошків ZrO_2, стабілізованого Y_2O_3 (YSZ), у діапазоні температур 80—350 K. Встановлено, що ТСЛ у нелегованому ZrO_2 зумовлена переважно власними дефектами, у легованому оксиді цирконію – домішковими дефектами. З використанням методу початкових нахилів розраховані значення енергій активації пасток досліджуваних зразків YSZ. Запропоновано модель ТСЛ YSZ.