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Studying the Thermostimulated Luminescence of the Gd_2O_2S: Tb and Y_2O_2S: Tb Ceramics Compounds under the X-Ray Excitation

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☐ ABSTRACT ☐

In this paper, we discuss the results of the luminescence properties of gadolinium and yttrium oxysulphides doped with terbium. These materials are known as effective X-ray screen phosphors. Their applications are more accessible in a ceramic form. The emission spectra of the Gd_2O_2S: Tb and Y_2O_2S: Tb show lines which are associated with $^5D_3$ - $^7F_{J'}$ and $^5D_4$ - ^7F_J (J' = 0-6, J = 1-6) transitions in terbium. The decay time of the luminescence of these oxysulphides was found to be 200 μs. We found that new defects in the samples appeared after the ceramic formation in comparison with the initial powders. Energy levels of the defects were estimated using thermostimulated luminescence (TSL) measurements. The determined characteristics (light yield, relative concentrations of traps, transparency, and afterglow) of studying ceramics, depend on the pressure conditions and a thermal treatment. The ceramics light yield, was almost the same as that of the powders, despite of the new defects presence. powders were obtained despite the presence of new defects.

The measurements have been held in Tech-governmental University of Petersburg-Petersburg-Russia. In year 2003

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دراسة التألق الحراري لمركبات السيراميك
$(Gd_2O_2S:Tb \text{ and } Y_2O_2S:Tb)$ بتأثير أشعة (X)

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(قبل للنشر في 2005/12/15)

□ الملخّص □

نبين في هذا البحث مميزات التألق لأكاسيد مركبات الأيتريوم والكادولينيوم مع التيربيوم. تتصف هذه المواد بأنها فوسفورية حاجزة فعالة للأشعة السينية، وتطبيقاتها أكثر قبولاً على شكل مركبات السيراميك. ينتج طيف الإصدار لهذه المركبات: $(Gd_2O_2S:Tb \text{ and } Y_2O_2S:Tb)$ عن الانتقالات بين سويات الطاقة لـ: $(^5D_3 - {}^7F_{J'})$ و $(^5D_4 - {}^7F_J)$، حيث $(J' = 0\text{-}6, J = 1\text{-}6)$ هي انتقالات طيف الأيتريوم. وجدنا أن زمن التضاؤل التألقي لمركبات الأكاسيد الكبريتية هذه يصل إلى $/200\ \mu s/$.

تمت مقارنة أطياف هذه المركبات السيراميكية المشكلة مع أطيافها على شكل بودرة وإيجاد العيوب فيها. كذلك تم تقدير الخلل في سويات الطاقة باستخدام قياسات التألق الحراري التحفيزي (*TSL*). تبين أن مميزات (مردود الإصدار الضوئي التركيب النسبي–الشفافية لما بعد التألق) للمركبات السيراميكية المدروسة تتعلق بشروط الضغط والمعالجة الحرارية. غير أن مردود الإصدار الضوئي للسيراميك والبودرة هو نفسه تقريباً بغض النظر عن وجود بعض العيوب الجديدة.

أجريت القياسات التجريبية في جامعة بطرس بورغ التكنولوجية الحكومية – بطرس بورغ –روسيا. عام(2003)

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INTRODUCTION:

Gadolinium and yttrium oxysulphides doped with rare earth elements are widely used as effective cathode- and X-ray phosphors [1,2]. Moreover, the emission spectra of these materials have a long wavelength region, and therefore are matched well to silicon photodiodes [3]. A drawback of the oxysulphides is that they exist predominantly in a polycrystalline form, while large-size transparent samples are commonly used as scintillators. We can solve this problem by using these materials in a ceramic form. So we have studied the spectral lines and kinetic characteristics of the emission under the X-ray excitation of these ceramics. We varied the activator content, from(0.2-1.7 mass %), hot pressure and temperature (were used in a vacuum) to achieve better properties. LiF powder was added before pressing to get clear crystal and compact samples. The new defects appeared in ceramics compared with initial powders, the concentration and energy levels of the defects, were estimated by thermostimulated luminescence (TSL) measurements. Our results show that (in dependence of pressure conditions and the thermal treatment) we can get ceramics with properties as initial powders, and with new features. This work is devoted to the investigation of the defects, which appear after ceramic formation in comparison with the initial powder. We mostly pay attention to deep traps with energy levels more than 0.4 eV, because shallow traps were studied earlier by Yamamoto and Kano [4] in powder samples.

EXPERIMENTAL PROCEDURES:

The emission spectra have been measured at a steady state of X-ray excitation (45kV). Two photomultiplier tubes (PMT) at different wavelength regions, were used. At a short wavelength region it was PMT- 106 (200-680nm) and at a long wavelength region it was PMT- 83, (400-1100nm). In some cases PMT-106 was more preferred than PMT-83, because at the wavelength region 400-650 nm, PMT –106 is more sensitive. Monochromator MDR-2 was used with both PMTs with gratings 1200splits/mm for PMT-106 and 600 splits/mm for PMT-83 and FEU-106 photomultiplier, were used for the emission detection. The temperature was varied in 80-500 K range. All the spectra were compared with spectral sensitivity of a silicone photodiode. All kinetic measurements have been made using pulsed (less than 1 ns) X-ray source and standard START-STOP detection system. The description of this setup was published by Rodnyi et al. [5]. To determine the relative light output, two methods were used. In both cases a standard sample used was Csl:Tl. To obtain these data in the first method we compared the areas under the spectrum curves of the measured and the standard sample. In the second one, the number of counts (in 50 μs region for a measured sample and a standard one), were compared. For level of afterglow measurements, we used ultraviolet (UV) excitation (Hg-lamp), and the device for kinetic measurements. To determine the trap properties (such as energy levels, their relative concentrations), we used the thermo-stimulated luminescence (TSL) method. The TSL measurements were carried out after UV (exposure 2 min) or X-ray (exposure 10 min) excitations. The exposures were carried out at 295 K, and the curves were obtained at heating up to 600 k, with constant rate (this rate can be varied from 0.5 to 1.0 k/s.) (see Fig 1).

RESULTS AND DISCUSSION:

Yttrium and gadolinium oxysulphides doped with rare earth elements are widely used as efficient cathode-and X-ray phosphors. We have studied the ceramic Y_2O_2S: Tb and Gd_2O_2S:Tb samples. The spectra of these samples contained only lines associated with radiative transitions in that activators. We observed $^5D_3$-^7F_j and $^5D_4$-^7F_j (J= 1-6) transitions in that emission spectra (see Fig 2). This figure shows the transition lines spectrum at definite wave length for the Tb doped in the Ceramic. In this compound (we have studied) the kinetic measurements show decay time constants at range of 150-250 μs [6]. In this investigation we are primarily interested in the light yield output of these samples in comparison with Csl:Tl, and in the light yield output for photons which have the same direction with incident X-ray, and for photons which were emitted at the sample side opposite to the incident X-ray. The second point of our interest was the characteristic as afterglow. We separated the samples to a smallest level of afterglow, and to a highest light output. The technical conditions of the ceramic preparations, have been determined.

All the luminescence spectra have been measured under X-ray excitation (45kV) and at room temperature. We found that the spectra composition for ceramics do not differ from those for powder samples. They exhibit $^5D_3$ - ^7F_J and $^5D_4$ - ^7F_J (J = 1-6) transitions (*fig.3*).

The decay curves have been measured at a 50 μs time gate, as could be seen in *(fig.4)*. The decay times constants for different samples are in the range 150-250 μs. Our results differ from those of Shepherd et al [7] who obtained 0.7 ms using time gate in ms range.

Light yield measurements have been carried out with the same set up as for the kinetic measurements. We used two systems of light yields measurements: of the reflected photons – $I_{\text{reflected}}$ (incident X-ray and photons have the same direction), and the transmitted photons – $I_{\text{transmitted}}$ (incident X-rays and photons are at opposite sample sides). The Kodak powder screen Lanex Fine (Gd_2O_2S:Tb) was chosen as standard (100%). The results are presented in table 1.

Thermoluminescence measurement was carried out after X-ray exposure for 300 s (absorbed dose was about 100 mGy). For all samples (3-mm diameter, 1-mm thickness), the exposures were carried out at 295 k and glow curves are measured at heating up to 600 k with constant rate (the rate can be varied from 0.5 to 1 k/s). The results of the measurements were not corrected for the difference in the sample transparency. An example of TSL curve with one peak is presented in (*fig.5)*. For sample number 11, one can see an asymmetrical shape of the line. It is typical to the first order kinetic. For sample 11 we estimate the trap level E_t and frequency factor S by different methods:

1) By analysing an initial exponential growth.
2) By measuring glow curves at different rates (β= 0.5 k/s and β=1 k/s) and solving the system of the two equations $E_t/ KT_m^2 = (S/\beta) \exp(-E_t/kT_m)$ with different β and T_m values.
3) Using the half width ΔT and peak temperature T_m according to Chen's equations $E_t = 2.29\, KT_m^2 / \Delta T$ and $S= (2.29\beta/\Delta T) \exp(2.29T_m/\Delta T)$.

The first two methods give almost the same E_t value, of 0.51 eV and 0.49 eV, respectively, but the third method gives much larger value of 0.76 eV (the same for frequency factor S). In Table 1 all the presented results were obtained by the second method. The TSL measurement shows that the number of traps produced by hot pressing

(HP) depends strongly on F- contamination (samples 7-12). This effect is suppressed by the increase of Tb concentration (samples 4,5). It turns out that the optimal fluorine-contamination is 0.09%. An increase of F- contamination above this level, leads to generation of new traps.

We observed the same influence of F-contamination for the other set of samples (2,3), with larger initial powder grains and temperatures of HP. We observed less influence of HP temperature on trap generation in samples (5,6), but anyhow the trap concentration increases with the increasing of HP temperature at the same other conditions. An increase of the Tb concentration to 1% (samples 5,6) in $Gd_2O_2S:Tb$, did not give the significant light yield rise observed in $Y_2O_2S:Tb$ (sample 1). Yet transparent ceramics (samples 5,6,10,11) will be more efficient converters for γ_- quanta with energies> 100k eV.

CONCLUSIONS:

Our result show that the characteristics of some studied scintillators can be improved. Therefore, we have to choose optimal growth conditions, concentration of activator and co-activator, and the type of flux. Besides, we plan to vary the post-growth conditions, particularly at the cooling rate.

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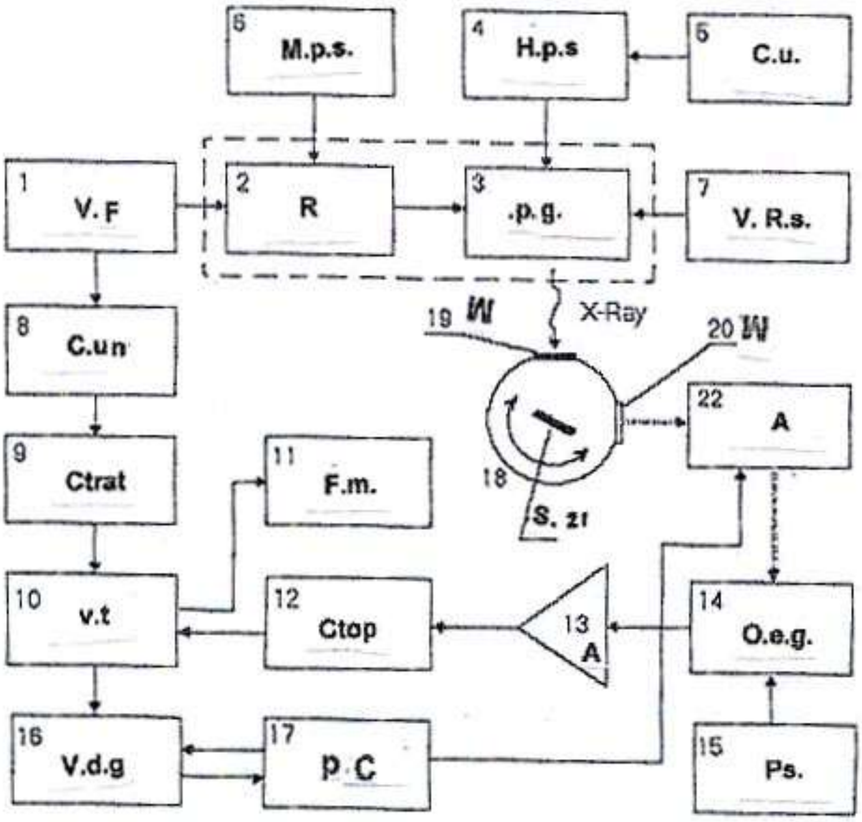

Fig 1: shows the instruments used for the measurement of the RL (X-Ray luminescence), TSL (Thermoluminescence)

1-Variable frequency generator.
2- Rheostat.
3- X-Ray pulses generator.
4- High power supply.
5- Control unit.
6- Modulating power supply.
7-Variable power supply.
8-Cut universal.
9-Time control connected to channel CTRAT.
10-Variable time modulator.
11- Frequency measuring.
12- Time control connected to channel CTOP.
13- Amplifier.
14-Optical electron generator.
15-Power supply for optical electron generator.
16- Variable digital analyzers.
17- IBM PC computer.
18-Cryostat.
19-Windows for cryostat Of Beryllium.
20-Quarts windows.
21- Sample.
22- Analyzer.

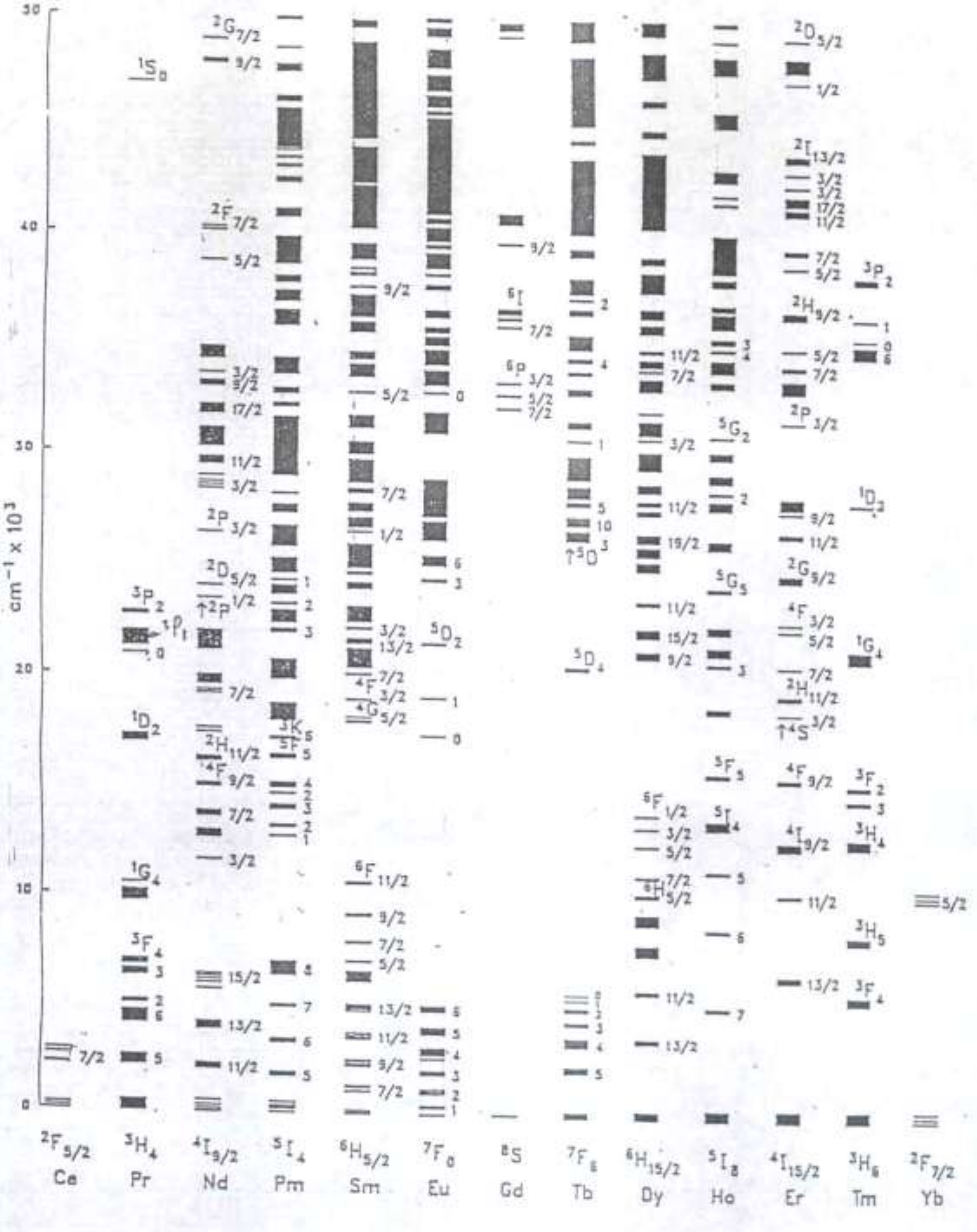

Fig 2 ENERGY LEVELS OF THE +3 LANTHANIDES IN LaF_3

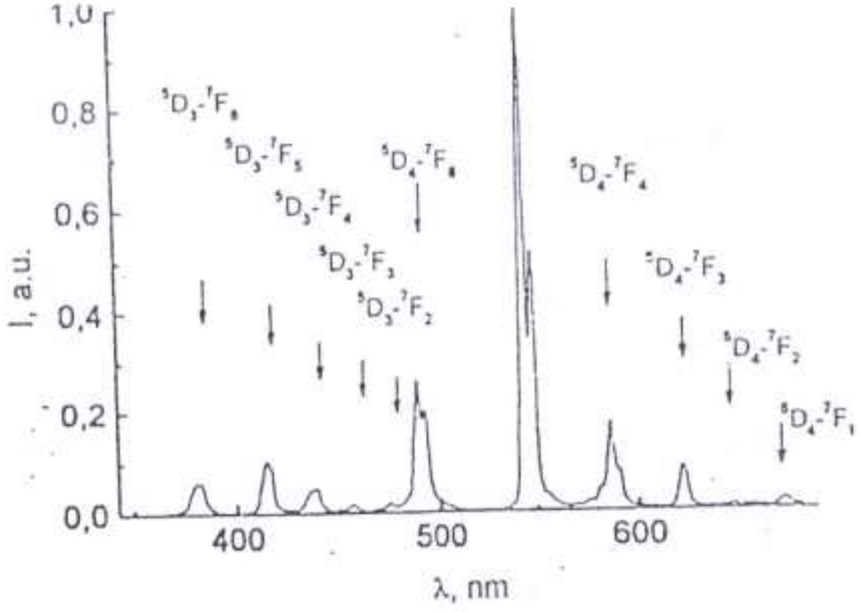

Fig. 3 *Emission spectra of the samples at X-ray excitation.*

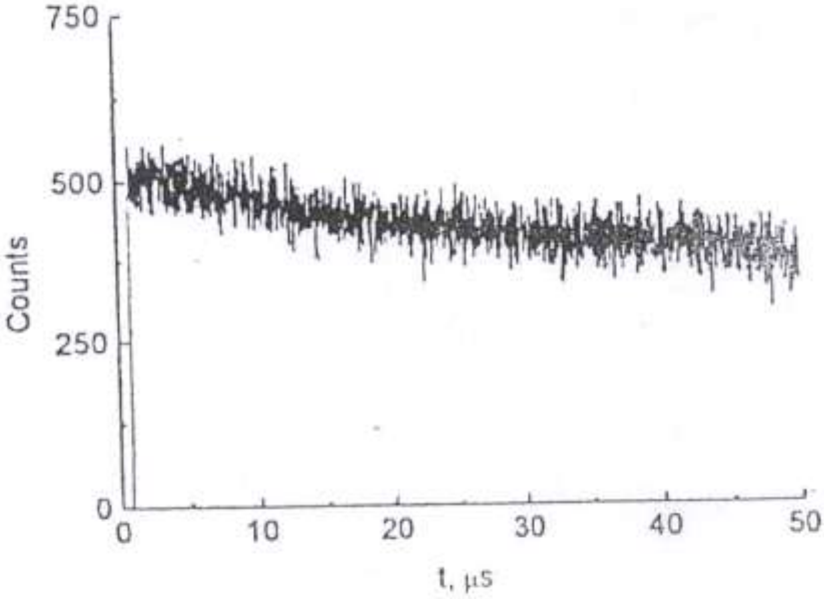

Fig. 4 *Decay curve of sample №1.*

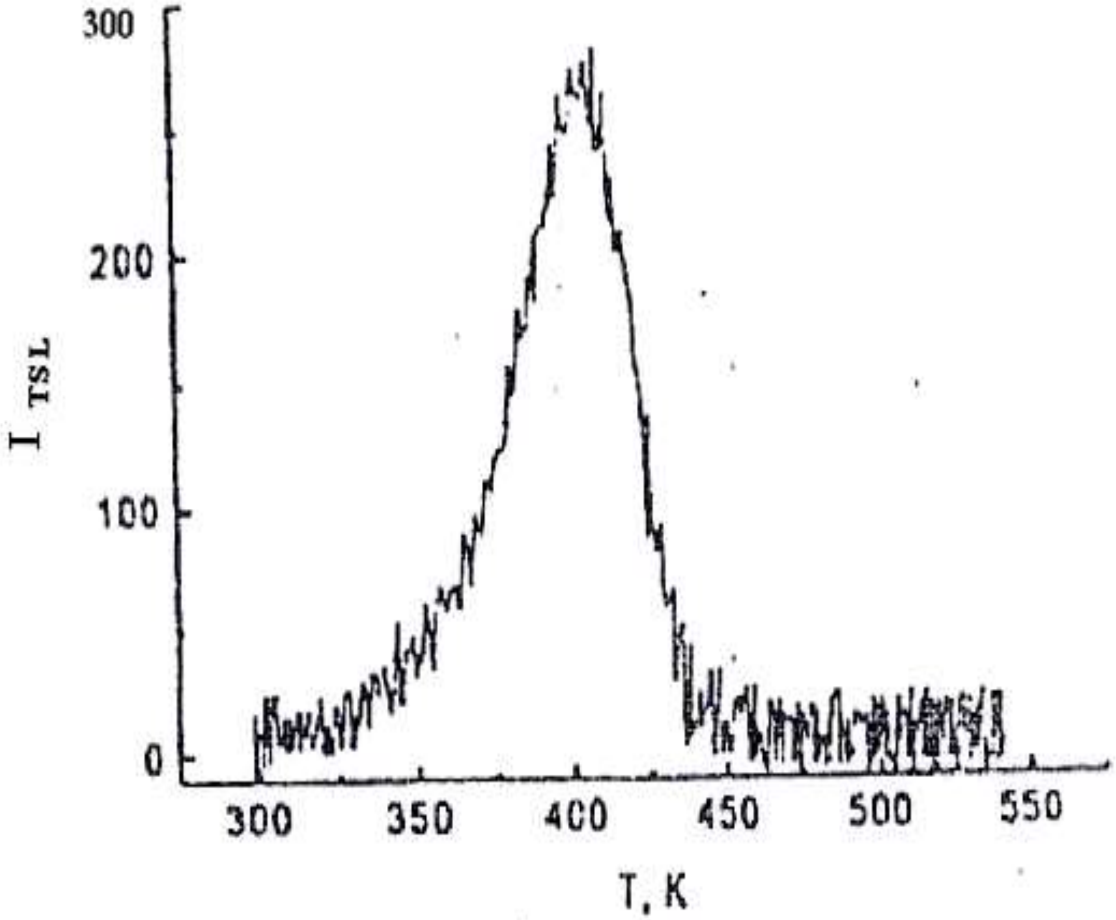

Fig ^{5} *TSL curve for sample N.11*

Table 1: Light yield, trap properties obtained from TSL measurements and some technical characteristics for some ceramic samples.

N°	Tb (mass%)	F (mass.%)	T_{hp} (k)	I_{ref} (a.u.)	I_{tran} (a.u.)	T_m (K)	E_t (eV)	S (s^{-1})	I_m (a.u.)
Kodak	-	-	-	100	58	-	-	-	-
Y_2O_2S									
1	2.5	0.1	1450	121	121	320 360 460	0.31 0.40 0.64	$1.1.10^6$ $9.6.10^6$ $2.0.10^9$	130 150 15
Gd_2O_2S									
2	0.03	0.1	1550	32	75	400	0.49	$8.1.10^7$	50
3	0.03	<0.01	1550	105	4	370 460	0.42 0.64	$1.6.10^7$ $2.0.10^9$	1900 10
4	1	<0.01	1550	68	3	400	0.49	$8.1.10^7$	6
5	1	0.1	1550	24	57	350	0.37	$5.6.10^6$	96
6	1	0.1	1500	29	63	380	0.44	$2.8.10^7$	2
7	0.03	<0.01	1500	132	4	360 400	0.40 0.49	$9.6.10^6$ $8.1.10^7$	2600 950
8	0.03	<0.01	1500	132	4	360 40	0.44 0.77	$2.8.10^7$ $1.4.10^8$	4000 3000
9	0.03	0.087	1500	29	55	380	0.44	$2.8.10^7$	15
10	0.03	0.089	1500	37	59	370	0.42	$1.6.10^7$	5
11	0.03	0.1	1500	34	61	406	0.50	$1.1.10^8$	250
12	0.03	0.13	1500	14	53	350 400	0.37 0.74	$5.6.10^6$ $8.1.10^7$	530 440

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