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Synthesis and Thermoluminescence Studies of Dy^{3+} Doped Bi_2O_3 Nanophosphors

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ABSTRACT
Detailed Thermoluminescence studies of Bi_2O_3 doped with Dy^{3+} synthesized by solution combustion method and irradiated with -rays and β-rays for doses in the range from a few Gy to KGy was done in the current work. Powder X-ray diffraction (PXRD) analysis is used to calculate the average particle size and was determined to be in the range 13-30 nm. Thermoluminescence (TL) characteristics of β-rayed Bi_2O_3: Dy^{3+} doped samples for dose of 1 Gy to 20 Gy are studied. In all -irradiated Bi_2O_3 : Dy^{3+} doped samples, at ~145 °C (T_{g1}) and ~155 °C (T_{g2}) two significant and well resolved TL glow peaks were observed. Also, the TL intensity is found to increase with dopant concentration up to 5 mol % and then decreases due to quenching. The peak position of both the glow peaks (T_{g1} and T_{g2}) is almost stable for the complete dose range. The activation energy and frequency factors are found to be 0.79 eV and 1.75×10^{15} s^{-1} respectively. These values are in very good agreement with those values calculated by peak shape methods and are found to be 0.73 eV and 1.70×10^{15} s^{-1} respectively.
Keywords— Bi_2O_3:Dy^{3+}; Thermoluminescence; Activation energy; Frequency factors

1. Introduction

Nanophosphors (NPs) doped with Lanthanide (Ln^{3+}) ions have gained substantial interest owing to their potential applications in diverse fields ranging from solar cells [1], remote photo activation [2], display [3], bio- imaging [4], drug release [5], solid state lasers [6], and temperature sensors [7] Besides, NPs should possess advanced physicochemical characteristics, such as low toxicity, high resistance to photo bleaching, high penetration depth, long lifetimes, as well as great anti- Stokes shifts[8]. The only nontoxic heavy metal that can easily be purified in large quantities is Bismuth [9].

The semiconductors such as Bi_2O_3 , BiOX (X= Br, Cl, I), Bi_2MoO_6 and $BiVO_4$ have a high refractive index and exceptional properties for photoluminescence, visible light absorption, dielectric permittivity, large oxygen ion conductivity, photoconductivity, and, notable, for photocatalytic activity. [10-13].

Among these semiconductors, the semiconductor with significant optical and electronic properties is Bismuth oxide (Bi_2O_3). Because of these properties, Bi_2O_3 has become a vital material for various applications such as photocatalysts [14], gas sensors [15], fuel cells [16], and electronic components [17]. Bi_2O_3 has 5 polymorphic forms (α, β, γ, δ and ω) with varied structures and properties [18], among which monoclinic α and face-centered cubic δ are stable at room temperature and at high temperature respectively. Bi_2O_3 NPs can be synthesized by various methods viz., sol-gel approach, micro-emulsion, sonochemical, hydrothermal, surfactant thermal strategy, chemical vapour deposition, solution combustion, microwave irradiation and electro-spinning [19].

In the present work the synthesis of $Bi_{2-x}O_3$: Dy_x (x= 0.01 to 0.11) NPs via effortless low temperature solution combustion method is reported. In comparison with conventional methods used for synthesis, the solution combustion method is beneficial with respect to low temperature and consumption of less time which yields in a high degree of crystallinity and homogeneity. The

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synthesised NP is characterized by PXRD. The effect of Dy^{3+} doping on the thermoluminescence properties was analysed in detail for their probable usage in display applications.

2. Experimental Methods or Methodology

2.1. Synthesis

For the low solution combustion method, analytical grade Bismuth nitrate ($Bi(NO_3)_3.5H_2O$: 99.99%, Sigma Aldrich Ltd.) as Oxidizer, Dysprosium nitrate ($Dy(NO_3)_3.6H_2O$: 99.99%, Sigma Aldrich Ltd) as dopant and Urea as fuel are used for the synthesis of $Bi_{2-x}O_3$: Dy_x (x= 0.01 to 0.11). The aqueous solution containing stoichiometric quantity of reactants are taken in a cylindrical Petri dish (300 ml), such that Oxidizer to Fuel ratio is 1 (O/F=1) and introduced into a pre heated muffle furnace at temperature of 400 ±10 °C. Nano powders are resulted by the thermal dehydration of the reaction mixture with the liberation of gaseous products. Finally, the nano powders were calcined at 600 °C for 3 h [20].

2.2. Characterization

PXRD using X-ray diffractometer (Shimadzu) (V-50 kV, I-20 mA, λ-1.541Å, scan rate of 2^{o} min^{-1}) was used to determine the Crystal morphology of the synthesised NPs. Thermoluminescence glow curves of β- and γ- rayed Bi_2O_3: Dy^{3+} doped samples are analysed using a TL setup consisting of a small kanthal heating strip, temperature programmer, photomultiplier tube (RCA931A),and a milli voltmeter (Rishcom 100) at a heating rate of $5^{o}Cs^{-1}$.

3. Results and Discussion

3.1. PXRD studies

Figure 1 shows the PXRD pattern of Bi_2O_3 NPs doped with Dy^{3+} (1-11 mol %). All the recorded peaks were indexed to the Cubic phase of Bi_2O_3 (JCPDS card No.52-1007, Space Group: Fm-3m (no.225)), signifying high purity and crystallinity of the synthesized NPs. Scherer's formula was used to determine the average crystallite size (D) [21]

$$D = \frac{0.9\lambda}{\beta\cos\theta} --- (1)$$

where 'λ'; wavelength of X-rays, and 'β'; Full width half maxima (FWHM) of XRD peaks. D value of Bi_2O_3:Dy^{3+} (1-11 mol %) samples lies in the range 13-30 nm which indicates that, the value of D decreases with the increase of doping concentration, which is due to the fact that the addition of Dy^{3+} ions decreases the gap between conduction and valence bands.

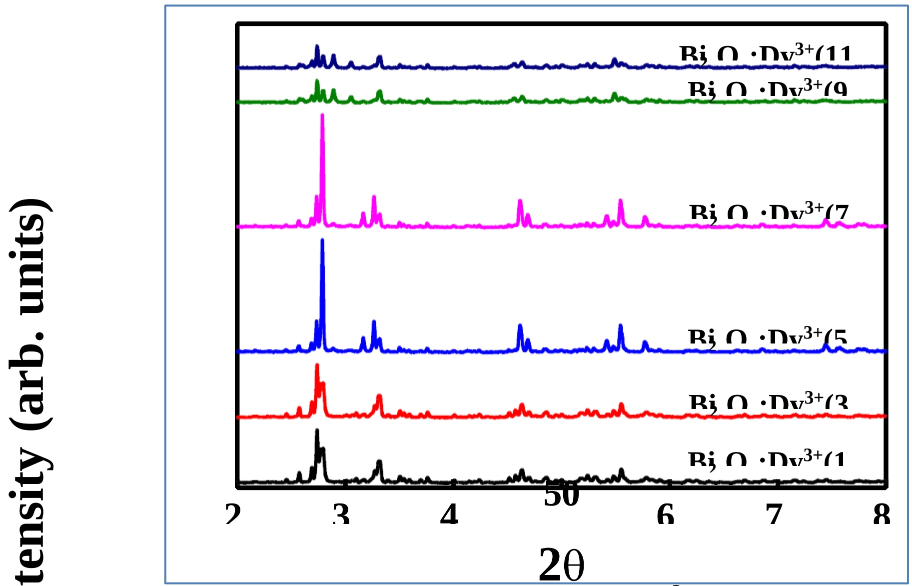

Fig. 1: PXRD of Bi_2O_3 NPs doped with Dy^{3+} (1 to 11 mol %)

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3.2. Glow curves of Bi2O3: Dy^{3+} (5 mol %)

Figure 2 shows the TL glow curves of Bi2O3: Dy^{3+} (1-9 mol %) gamma rayed for dose 1 kGy. The glow curves clearly shows two prominent and well resolved glows with peaks at ~ 145 °C (Tg1) and
~ 155 °C (Tg2) along with a shoulder peak at ~ 163 °C. It also shows that TL intensity increases almost linearly with increase in gamma ray dose upto 5 mol % and then decreases for higher mol concentration of Dy. The decreases in intensity may be due to quenching. The peak position of TL glow for both Tg1 and Tg2 is almost stable for the complete dose range. The intensity of TL glow peak decreases at higher concentration of dopant ions and this might be probably due to the occupancy of deep traps and also due to disorganization of the initial energy levels. The variation of glow peak intensity and position as a function of concentration is shown in figure 3 [22, 23]. The kinetic parameters were determined according to glow curve shape method (modified by Chen) using CGCD as shown in Figure 4 and results are tabulated in Table 1. TL glow peak depends on a range of parameters such as history of the samples, heat-treatment of the samples preceding irradiation, physical nature of the sample, impurity content of the sample, nature and amount of dose given to the sample, temperature at which irradiation as well as TL measurements are made, environment of the sample while irradiation, rate of heating the sample etc.

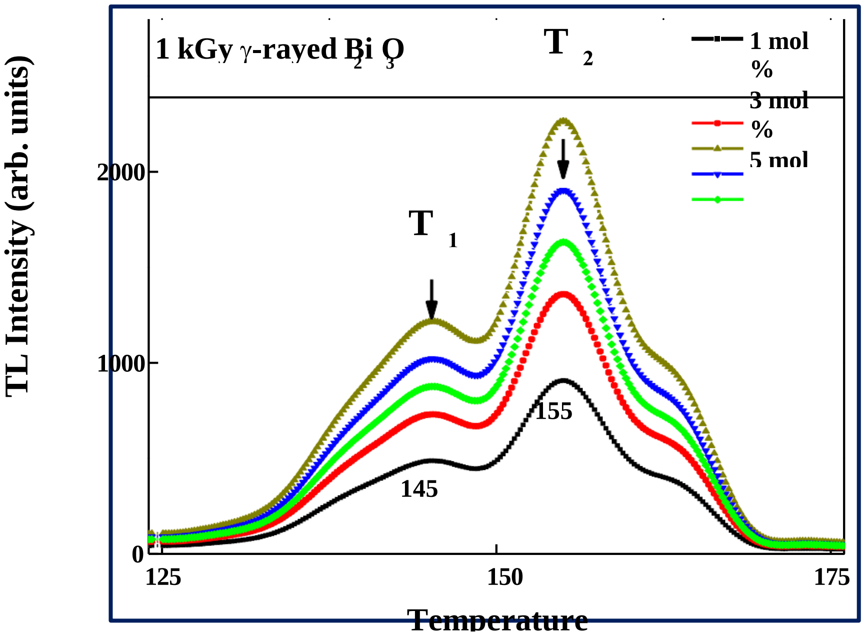

Fig 2. Thermoluminescence glow curves in γ-rayed Bi2O3 nanocrystals (β=5°Cs^{-1}).

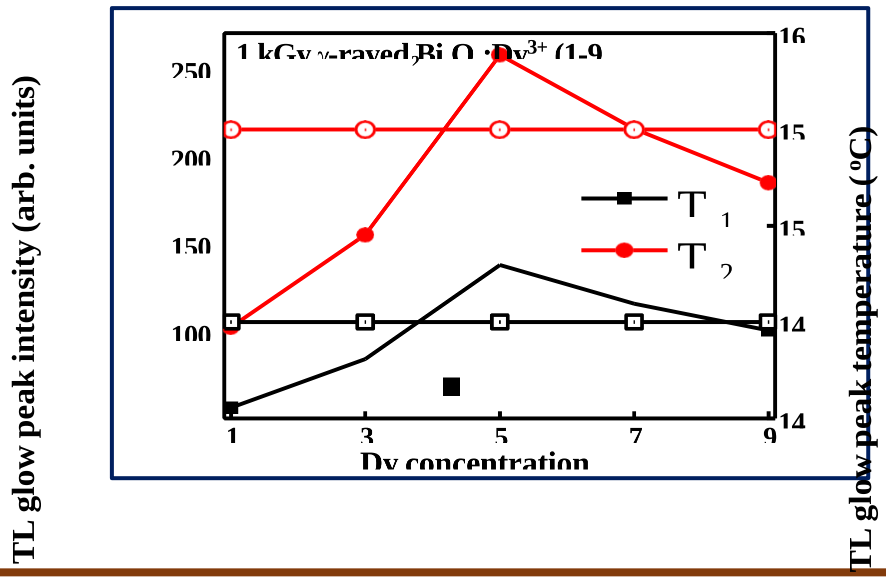

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Fig 3. TL glow peak intensity and temperature as a function of dose

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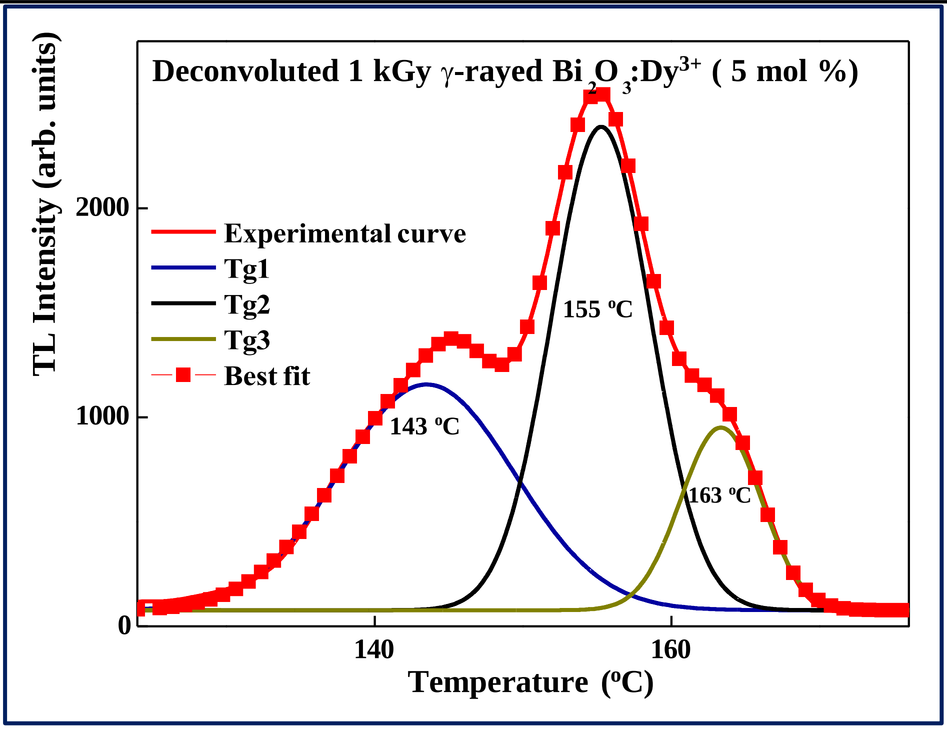

Fig 4. CGCD thermoluminescence glow curve γ- rayed Bi_2O_3: Dy^{3+} (5 mol %)

Table 1. TL kinetic parameters of Bi_2O_3: Dy^{3+} irradiated with γ-rays for 1 KGy obtained by the glow curve shape method (modified by Chen).

Glow Peak temperature, T_m(°C)	Glow peak parameters				TL parameters		
	δ (°C)	τ (°C)	ω (°C)	μg	Et (eV)	no (cm^{-3})	S (s^{-1})
143	7.05	7.1	14	0.5	0.929	980	$8.42x10^{13}$
155	4	3	7	0.45	0.73	1294	$1.70x10^{15}$
163	4	3	7	0.44	0.815	515	$5.12x10^{16}$

The influence of different heating rates from 5 °C/s to 40 °C/s on the TL response has been carried out for Bi_2O_3: Dy^{3+} (5 mol %). It was found that as heating rate increases, the peak intensity and the total area of the main peak decreases where as the peak temperature (T_m) moves towards higher temperature. This may be attributed to the thermal quenching of TL. Fig 5 shows TL glow curves of Bi_2O_3: Dy^{3+} (5 mol %) γ-rayed for 1 kGy at different heating rates (β). It is seen that with the variation in heating rates, peak shape varies and there is a shift in the peak position. This can be explained as follows. At low heating rate the time spend by the phosphor is large enough so that certain quantity of thermal release of electrons depending on the half life at this temperature could take place. Now, as the heating rate increases the time spend at the same temperature decreases and hence the thermal release of electrons is also decreased. So, a much higher temperature is required for the same amount of thermal release to happen. In this manner the whole glow peak is shifted to higher temperature as the heating rate increases in a way depending on the half life and the time spent at each temperature [24].

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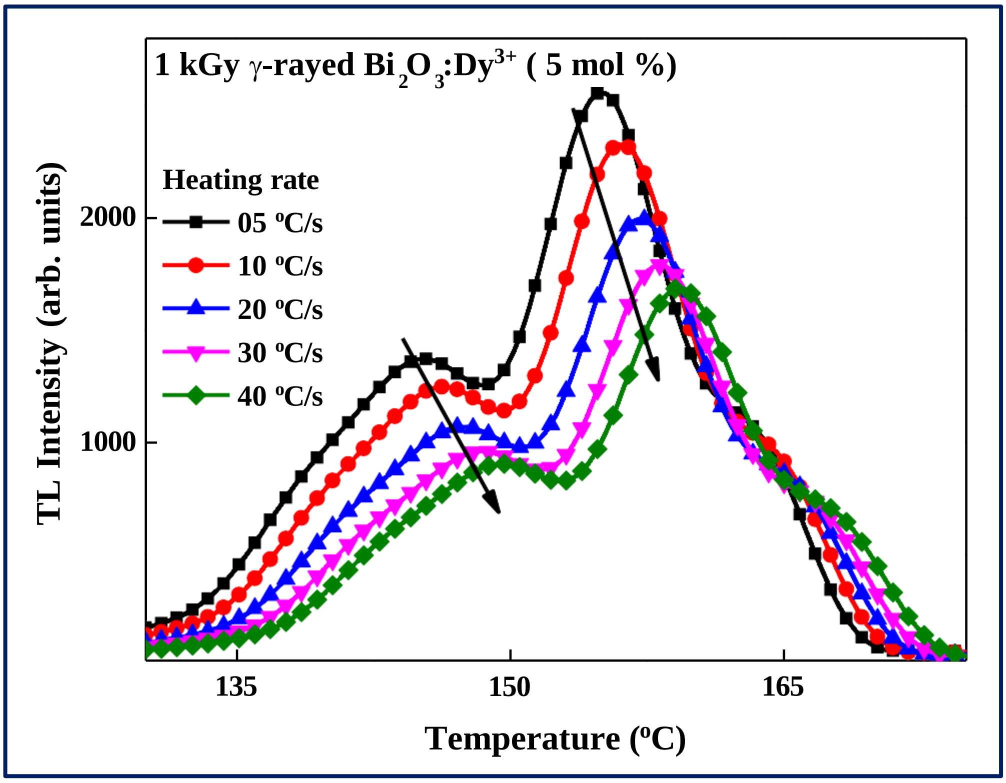

Fig 5 Thermoluminescence glow curves of Bi2O3: Dy^{3+} (5 mol %) γ-rayed for 1 kGy at different heating rates (β)

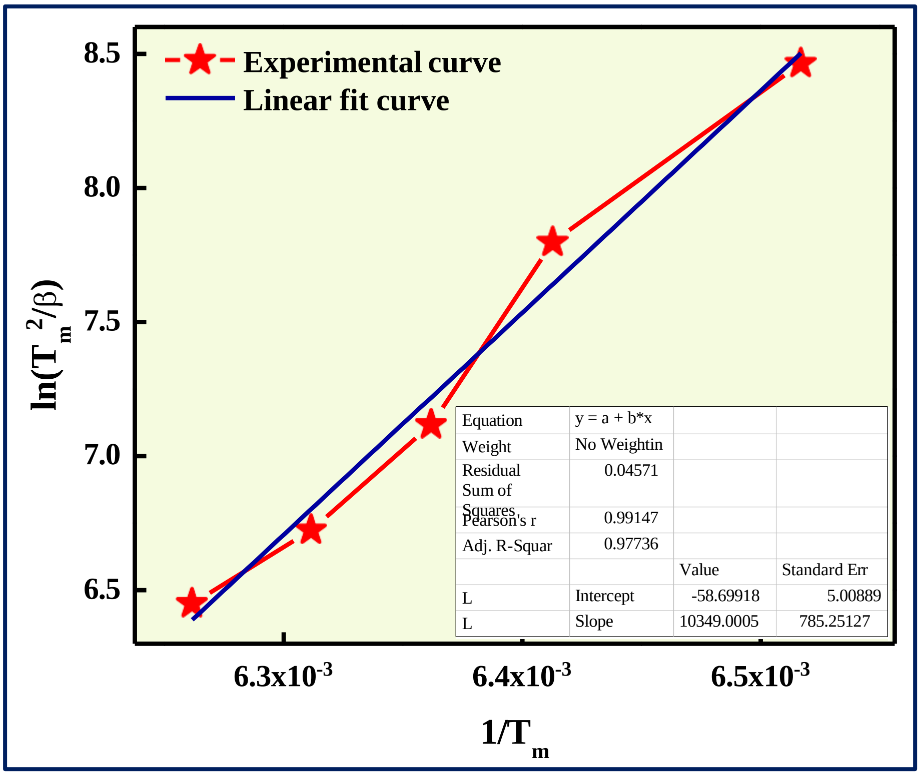

Fig 6. Variation of ln (T_m^2/ β) v/s 1/T_m in TL glow curves of Bi_2O_3 : Dy^{3+} (5 mol %) γ-rayed for 2 kGy at different heating rates (β)

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The variable heating rate (VHR) method is used to find the trapping parameters as given by Chen et al and Yazici et al [25,26]. According to them a $\ln(T_m^2/\beta)$ against $1/T_m$ gives a straight line with slope equal to E/k, where 'k' is the Boltzmann constant, 'E' trap depth. Extrapolation of straight line to $1/T_m = 0$ gives a value of (s k/E) from which the frequency factor 's' can be found by insertion of E/k found from the slope. Figure 6 shows the plot of variation of $\ln(T_m^2/\beta)$ v/s $1/T_m$ in TL glow curves of Bi_2O_3: Dy^{3+} (5 mol %) γ-rayed for 1 kGy at different heating rates (β). From the plot, the activation energy and frequency factors are found to be 0.79 eV and 1.75×10^{15} s^{-1} respectively. These values are in very good agreement with those values calculated by peak shape methods where the activation energy and frequency factors are found to be 0.73 eV and 1.70×10^{15} s^{-1}.

The behaviour of FWHM is an outcome of the whole glow peak shift versus heating rate since it is measured as a temperature difference within the glow peak region. Thus it is precisely same as that of T_{max}. Similar results were observed by Gorbics et. al [27] where a decrease of both integral and peak height happens and the glow peak shifts to higher temperatures due to thermal quenching. Taylor and Lilley [28] experimented a reduction in TL intensity of LiF at high heating rates.

The phenomenon of the decrease in the TL intensity with heating rate is a universal one. This was observed in various materials and is independent of the nature of specific impurity. For all these observations, the back ground under each glow peak was kept zero for all heating rate, i.e., the thermal release of trapping species is complete. Hence we can assign the decrease in TL intensity to the recombination process, i.e., trapping species in the conduction band and luminescence centers. As carrier pile up is lined out at these heating rates, the reduction in the normalized TL is due to thermal quenching of the luminescence centers. The increase in the glow peak temperature with increase of heating rate for recording the TL signal is a universal phenomenon [29,30].

CONCLUSION

Detailed Thermoluminescence studies of Bi_2O_3 doped with Dy^{3+} and Sm^{3+} synthesized by solution combustion method and irradiated with □-rays and β-rays for doses in the range from a few Gy to KGy was done in this chapter. In all □-irradiated Bi_2O_3 : Dy^{3+}doped samples, two prominent and well resolved TL glow peaks at ~145 °C (T_{g1}) and ~155 °C (T_{g2}) are observed. Also, the TL intensity is found to increase with dopant concentration up to 5 mol % and then decreases due to quenching. The peak position of both the glow peaks (T_{g1} and T_{g2}) is almost stable for the complete dose range. The increase in TL glow peak intensity initially may be due to the occupancy of deep traps and it may be attributed to disorganization of the initial energy levels as a result of high dose.

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