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Kinetic Characterization and T L Studies of $(ZnS)_{1-x}(MnTe)_x$ Nanophosphors

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ABSTRACT

In the present paper we analyze the kinetics involved in experimentally reported thermoluminescence study of wet chemical synthesized $(ZnS)_{1-x}$ $(MnTe)_x$ nanophosphors. There are two peaks in the rmoluminescence glow curves and corresponding order of kinetics parameter are evaluated. Here we use a new method of analysis after discussing the shortcomings of already used method. As per the new method of analysis, the activation energy and escape frequency factor parameters are characteristic parameters of the specimen and order of kinetics parameter depends on experimental conditions. Effect of size of specimen on activation energy, escape frequency factor and peak temperature are also discussed.

KEYWORDS: The rmoluminescence, Nanophosphors, Order of Kinetics, Activation Energy, Escape frequency factor.

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INTRODUCTION

Nanophosphors are inorganic insulating materials and are nanostructured form of existing phosphor materials. The semiconductor nanocrystals show a variety of unique optical, electronic and chemical properties which originate mainly due to two reasons, i.e., quantum confinement effects and large surface to volume ratio. In recent years, the luminescent nanocrystals, also termed as nanophosphors, attracted considerable interest after the observation of enhanced luminescence efficiency and shortening of radiative lifetime by orders of magnitude from milliseconds to nanoseconds when compared with the bulk counterparts. These promising properties along with the possibility of synthesizing such materials by wet chemical methods will bear a great potential for their applications in a number of high technology areas such as high density displays, bio-markers, lasers, sensors, etc. If an insulator or semiconductor is previously exposed to radiation and then heated, the energy stored in the phosphors as a result of irradiation process liberates in addition to the normal thermal radiation. The additional radiation emitted during first heating of the material is called thermally stimulates luminescence (TSL) or simply thermoluminescence (TL). When an irradiated coloured crystal is heated, holes or electrons are set free from the traps (defect sites) and emission takes place when they recombine with charges of opposite sign. On the other hand, defect sites which release the carriers are known as traps. In contrast, the centers from where the thermal release of carrier, etc. are not possible, but where the probability of capture of a charge of opposite sign is appreciable, are called recombination centres. Thermoluminescence is a very thirsty area of research because of its immense contribution in the fields of personnel and environmental dosimetry, dating of archaeological artefacts, sediments and study of defects in solids[1,2,3,4,5]. The thermoluminescence study of ZnS nanoparticles show that the TL intensity increases as the particle size is decreased[6]. Smaller particles have larger surface to volume ratio and more accessible carriers for TL. Also, the carrier recombination rate increases upon decreasing size due to the increase of the overlap between the electron and hole wave functions. These two effects may cause TL to increase with decreasing the size of particles. Shape of TL glow curve of this nanophosphor is not affected by the size of the particles during the growth of nanophosphors whereas its TL intensity was highly increased with a decrease in the size of particles[7]. In addition Sharma et al.[8] also reported shift in peak position with decreasing size of nanoparticles.

The present paper reports the kinetic analysis of experimentally reported Thermoluminescence data of $(ZnS)_{1-x}(MnTe)_x$ nanophosphors prepared by wet chemical method[9].

METHOD OF ANALYSIS

Adirovitch[10] proposed a set of three equations, which controls the traffic of electrons from the trap centre to the recombination centre via conduction in the rmoluminescence (TL) process and the TL intensity (I) at any temperature (T) is given by relation[1,11]

$$I = n_0\, s \exp[\, -\frac{E_a}{k\,T} - \frac{s}{b} - \int_{T_0}^{T} (\, -\frac{E_a}{k\,T'}) \, dT' \,] \qquad \ldots (1)$$

where n_0 is the initial concentration of the trapped electrons per unit volume at T_0, which is the initial temperature wherefrom the TL glow curve starts to appear, s is the pre-exponential factor or escape frequency factor, E_a is the activation energy or trap depth, k is the Boltzmann's constant, b is linear heating rate and T' is an arbitrary temperature in the range T_0 to T . The peak temperature relation is given by relation

$$T_m^2 = \frac{b\, E_a\, \tau_m}{k} \qquad \ldots (2)$$

Where T_m is temperature corresponding to maximum TL intensity and τ_m is relaxation time at Tm and is given by Arrhenius relation[12] as

$$\tau_m = \tau_0 \exp(\frac{E_a}{k\, T_m}) \qquad \ldots (3)$$

Where τ_0 is fundamental relaxation time and is related with pre-exponential factor or escape frequency factor as

$$\tau_0 = \frac{1}{s} \qquad \ldots (4)$$

Pateria et.al.[9] from their experimental study of thermoluminescence of wet chemical synthesized $(ZnS)_{1-x}(MnTe)_x$ nanophosphors, evaluate the activation energy using the relation

$$E_a = \frac{2\, k\, T_m^2}{\delta} \qquad \ldots (5)$$

where $\delta = T_2 - T_m$, T_2 is the temperature to higher temperature side of full- width half- maxima. The escape frequency factor is evaluated using the relation

$$s = \frac{b\, E_a\, e^{\frac{E_a}{k}Tm}}{T_m^2} \qquad \ldots (6)$$

The reported values are shown in Table.1. Equation (2) for the peak temperature is generally accepted by all researchers engaged in same work. But in the present from 5th and 6th columns of Table.1 it is clear that reported values of peak temperature, activation energy and escape frequency factor do not satisfy eq.(2).

In order to remove this inability, here we reconsider the mechanism proposed by Prakash[13]. In his proposed mechanism he reasonably and logically modify the Adirovitch set of equations, and establish a relation for intensity of TL glow curve as

$$I = (1-x)n_0\, s \exp[-\frac{E_a}{k\,T} - \frac{s\,(1-x)}{b}\int_{T_0}^{T}\exp(-\frac{E_a}{k\,T'})\,dT'\,] \quad \ldots. \quad (7)$$

and the peak temperature is given by

$$T_m^2 = \frac{\ell\, b\, E_a\, \tau_m}{k} \quad \ldots (8)$$

where x is extent of retrapping involved in TL process which is related with order of kinetics (ℓ) parameter as

$$\ell = \frac{1}{1-x} \quad \ldots (9)$$

RESULTS AND DISCUSSION

Following the above discussed new method of analysis, order of kinetics parameter is evaluated and are given in Table.1. It has been observed that ℓ is different for different peaks as well as for different dopant concentrations. TL is measured to obtain useful information about the surface states of the particles. TL occurs due to detrapping of carriers caused by heating the samples. As the size becomes smaller, the surface to volume ratio increases, and the particles contain more accessible carriers for TL. This is one factor to make the TL increase upon decreasing size.

Table.1 Experimentally reported values of T_m and E_a [9] and evaluated values of ℓ.

Phosphors	T_m (K)	E_a (eV)	τ_0 (s)	T_m^2 (K^2)	$\frac{b\,E_a\tau_m}{k}$ (K^2)	ℓ
$(ZnS)_1$-x(MnTe)x, x=0.02	378.0	0.4636	2.04E-12	142884	0.16668311	857219.4
	456.5	0.7626	1.01E-14	208392.3	0.23483645	887393.1
$(ZnS)_1$-x(MnTe)x, x=0.05	377.0	0.4612	2.13E-12	142129	0.16674277	852384.8
	455.6	0.7592	1.05E-14	207480.3	0.23313125	889971.9
$(ZnS)_1$-x(MnTe)x, x=0.10	376.0	0.458	2.22E-12	141376	0.16270955	868885.7
	454.6	0.7559	1.08E-14	206570.3	0.22742489	908301.0
$(ZnS)_1$-x(MnTe)x, x=0.15	375.0	0.4563	2.27E-12	140625	0.16333564	860957.2
	453.6	0.7526	1.18E-14	205662.3	0.23758045	865653.1
$(ZnS)_1$-x(MnTe)x, x=0.20	374.0	0.4539	2.38E-12	139876	0.16407765	852498.8
	452.6	0.7493	1.22E-14	204756.3	0.23509084	870966.5
$(ZnS)_1$-x(MnTe)x, x=0.25	373.0	0.4515	2.44E-12	139129	0.16113218	863446.4
	451.6	0.746	1.27E-14	203852.3	0.23289119	875311.1

The glow peak of the particles is sensitive to the size, in which the trap depth decreases with reducing size of the nanoparticles. The wave functions of electrons and holes are effectively overlapped in nanoparticles, and this may also cause increase in their recombination probability. The TL of small nanoparticles is expected to be more than that of the bulk. The separation between the electron–hole states (similar to the donor–acceptor pairs) increases with the decreasing size of the nanoparticles because the trap-depth does not change much upon decreasing size, while the bandgap

increases . In the case of material under consideration also the trap depth should not change significantly with increasing size of the nano-phosphors.

CONCLUSION

With the help of a Prakash method of analysis, order of kinetics parameter is evaluated from reported values of activation energy and escape frequency factor. This parameter depends on extent of retrapping involved in thermoluminescence process. As the smaller particles have higher surface/volume ratio and more surface states, they contain more accessible carriers for TL. Furthermore, the carrier recombination rate increases with reducing size of the nanocrystals because of the increase of the overlap between electron and hole wave functions. As a consequence of these two effects the TL intensity increases upon decreasing size of the nanoparticles. Some decrease in the activation energy can be obtained with reducing size of the nanoparticles and vice-versa. Escape frequency factor decreases with reducing size of nanoparticles. It is to be noted that, although both activation energy and peak temperature decrease with reducing size of nanoparticles, the ratio of these two decreases with reducing size of the nanoparticles because decrease of activation energy with reducing size of nanoparticles is comparatively faster as compared to the decrease of peak temperature with reducing size of nanoparticles.

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