



## **Intricacies of Thermoluminescence in Sulphate based Phosphors from a Historical Perspective**

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### **1. HISTORICAL**

When I joined Division of Radiological Protection, BARC, Mumbai in December, 1971 as a junior scientific officer, the first problem assigned to our group headed by Dr. Komanduri Ayyangar who just returned from USA and consisted of eminent scientists Dr. Bhuwan Chandra Bhatt and Dr. Ambika Shai Pradhan was the development of a personnel monitoring badge based on thermoluminescent dosimeter (TLD) since the AgBr emulsion based Film badge used so far fades at high humidity and temperatures. At that time, the film badge lobby was very powerful but they had to accept the bare reality that the film badge exposed at 95% RH showed no signal at all. At this time, Dr. Krishna Gopal Vohra became the new Head of DRP. He had a pivotal role in the development of the TLD badge which is widely used presently in India not only in nuclear installations but also in hospitals.

By that time high sensitive, stable and reliable  $\text{CaSO}_4:\text{Dy}$  TL phosphor has been made by us based on Japanese Yamashita's recrystallization technique [1] which consisted of complete evaporation of hot sulfuric acid which gives hazardous fumes. Dr. B.C. Bhatt and myself had the dubious distinction of corroding many fume hoods at Modular Laboratories in BARC. The other problem which had to be overcome was the development of this phosphor in solid form. Incidentally the powder filled glass capillary tubes developed by Dr. Pradhan which was used to measure radiation levels in the Pokran test (Dr. D.V. Gopinath came suddenly to DRP one day and took away all the phosphor filled capillary tubes available at that point of time without telling any reason!) was not considered good enough for routine personnel monitoring. The two options discussed were to import the entire system, both TLDs and the reading equipment from companies like Harshaw, USA. But Dr. Ayyangar with his vast experience and wisdom resisted this idea and instead suggested we could go in for PTFE (Teflon) based  $\text{CaSO}_4:\text{Dy}$  badge as the phosphor recipe is known. At that time, we did not even know how to mix the nonfree flowing PTFE (Dupont's 7A grade) powder with free flowing  $\text{CaSO}_4:\text{Dy}$ . Extrusion of PTFE filled powder with a machine made by Dr. K. Ayyangar did not work. It was

Dr. K.G. Vohra who came up with two brilliant ideas to solve these two outstanding issues. During a car ride with Dr. Vohra to Malabar Hills after the office hours, Dr. B.C. Bhatt and myself expressed the difficulties faced by us in acid evaporation. Immediately he said that he will write to Dr. Karakanwalla, Head, Chemistry Division to sort out this issue. His colleagues subsequently came up with a closed acid evaporation set-up which is being used presently. The acid fumes were condensed into a beaker with water cooling and this system was capable of making large batches (300 g size) of  $\text{CaSO}_4:\text{Dy}$  TLD phosphor without letting the acid vapor into the atmosphere. The other problem of mixing was also sorted out by Dr. Vohra who suggested the use of cryogenics which was being used in Air Monitoring section, BARC to pound polyethylene powder. Immediately we took up this idea and succeeded in mixing uniformly the  $\text{CaSO}_4:\text{Dy}$  powder with PTFE powder since the later became free flowing in liquid nitrogen. After cold pressing manually, the discs could be sintered at  $400^\circ\text{C}$  to impart sufficient strength. At the suggestion of Dr. Vohra, all three of us visited a pharmaceutical machine manufacturer in Mumbai to see if their parallelization machine could be used to manufacture automatically TLD Teflon discs. But it did not work since ours was a non free flowing powder whereas medicinal powders are free flowing. So even today TLD discs are hand pressed manually. After the migration of Dr. Ayyangar to USA in 1974, Dr. R.C. Bhatt was chosen, after much consultations, to head this active research group on TLD which came up with many research publications in subsequent years. Only after the development of TLD badge we were allowed to do publication related research work. That was the discipline enforced by BARC in those days. I am proud to inform that we were one of the earliest to use PTFE in India. I continued to work on it and recently developed successfully at Saveetha Engineering College for the first time in India the technology of recycling PTFE scrap without involving irradiation under a project funded by TePP, DSIR [2]. It is likely to be commercialized soon.

The initial resistance and hesitation in introducing TLD badge vanished when it successfully showed the presence of radioactive substance in Dr. Ramanna's (Director, BARC) drawer. Dr. Vohra could then easily obtain Director's approval to introduce TLD badge for country wide radiation monitoring [3]. Dr. K.G. Vohra took great care and pains in the design of TLD badge. The majenda

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color on the Aluminum filter in the badge was his choice. He usually comes to BARC with a majenda color shirt with a matching tie, the only one who comes to BARC with a tie at that time. He was so much devoted to the development of TLD badge and asked all of us to concentrate on it. I still recall two incidents, one involving Dr.B.C. Bhatt and the other myself. Once when Dr. Bhatt, to explain his absence on one day told him that guests have to his home, to which Dr. Vohra replied your Guests have come at the wrong time! Similarly when once I was returning from CC complex to Modular lab at the lunch time, he remarked why are you loitering here when there is so much of work there in the lab which brought tears in my eyes. At the same time he listens to good ideas. Initially the PTFE discs were glued to the TLD card with silicone resin but its adhesive strength was not strong. As a result, the discs started to fall inside the TLD reader during readout. Another problem faced with this adhesive was the cards could not be annealed beyond 200 deg C which resulted incomplete annealing of prior TL signal. As a result the environment low dose measurements in and around BARC made by me in the first run with the TLD badges were erratic. I then went to his room and boldly suggested only mechanical clipping will solve both these difficulties. Immediately he called Sri. Peerzada from the DRP workshop and assigned the problem to him who then came up with the present clipping design.

Despite competing developments such as optically stimulated luminescence based on  $Al_2O_3:C$ , DAE is sticking with the time tested  $CaSO_4:Dy$  TLD badge till today. I am very proud to inform that I am the first Ph.D student of Dr. Vohra in the field of TLD. He took great care in all of us. When I went on post-doctoral assignment to CERN, Geneva in 1982, he told Dr. Pradhan why are you still waiting here when your colleague is floating in money? Dr. Pradhan got subsequently post-doctoral assignment and went on to become a member of ICRP. Similarly Dr. Pradhan and myself became members of Editorial board at an young age in the prestigious Radiation Protection Dosimetry Journal published from UK under the patronage of Dr.K.G. Vohra. Those were the happier days in BARC. Dr. B.C. Bhatt. after superannuation became a DST emeritus scientist. The last time I met Dr. Vohra was during his brief visit to BARC from IAEA, Vienna. When I shook hands with him it was unusually warm. When I asked him if he was OK, he replied he is fine. But on return to Vienna he unfortunately expired due to Jaundice a tropical disease which was not diagnosed properly in Europe.

Parallel development took place in the instrumentation part thanks to the efforts of S. Kannan from DRP. The cards could be fed and read automatically and the contact ohmic heating was replaced by hot nitrogen heating which overcame contact problems. The phosphor and badge preparations as well as TLD reader manufacturing are then outsourced to private companies such as Renentech, Mumbai, Aventech, Chennai and Nucleonix, Hyderabad.

Prior to the above development, the Health Physics group headed by Dr.C.M. Sunta and Dr.K.S.V. Nambi employed natural  $CaF_2$  powder (Fluorite) for background radiation monitoring in coastal areas of Kerala. Dr. Ganguly, Director, Chemical Group took active interest in the research activities of TL. It was a pleasant experience to participate in group discussions extending to late night in early 70's in Modular Laboratories under Dr. Ganguly's leadership.

## 2. INTRICACIES OF THERMOLUMINESCENCE

### 2.1 Phosphor Preparation

Phosphor preparation is an art. For many applications, high sensitivity, low fading at room temperature and insensitivity to humidity are the main requirements. A review on  $CaSO_4$  based TLDs has shown that Dy and Tm are the best dopants since their excitation spectra overlaps well with the  $CaSO_4$  host emission peaking at about 350 nm [4]. Their main TL glow curve peaks at about 230°C which remains stable at RT for several months. Their TL emission spectra (480 and 540 nm for  $Dy^{3+}$  and 450 nm for  $Tm^{3+}$ ) match reasonably well with the spectral response of common photomultipliers used in the TLD reader. Their 3+ valence state is quite stable on irradiation. The phosphor could be reused a number of times after suitable thermal annealing. In contrast, red emission from  $Eu^{3+}$  (or  $Sm^{3+}$ ) does not match with the spectral response of blue sensitive photomultipliers. In addition the valence of  $Eu^{3+}$  in  $CaSO_4$  host is not stable. On irradiation and/or thermal anneal it gets partially converted to  $Eu^{2+}$ .which poses problems on their reusability.

Apart from recrystallization, several other techniques have been tried to make  $CaSO_4:Dy$ . These include solid state reactions at high temperatures, precipitation routes involving  $H_2SO_4$  or  $NH_4SO_4$ . All these techniques did not yield either the desired TL glow curve structure nor the sensitivity. One exception was the co-precipitation technique in hot  $H_2SO_4$  the dissolved constituents developed by the author's group at IGCAR [5]. This technique not only avoided the cumbersome procedure of lengthy acid evaporation but also yielded a phosphor with a higher TL sensitivity, desired glow curve structure and better phosphor grain morphology and size.

Other high sensitive phosphors such as  $BaSO_4:Eu^{2+}$ ,  $SrSO_4:Tb^{3+}$  could be developed easily by solid state reaction route at high temperatures. However, these phosphors did not catch up much attention perhaps due to their high effective atomic number.

Three important criteria to be considered in phosphor synthesis are: (i) the size matching between the host cation and impurity i.e  $Ba^{2+}$  and  $Eu^{2+}$  in the above case, (ii) their valence states (2+ in both cases is a preferred choice) and (iii) the electro-negativity (EN) of host should

be higher than that of the impurity (in this case both have the same value of 1). In contrast, in the case of  $\text{CaSO}_4:\text{Mn}$ , the EN of Mn (1.6) is higher than that of Ca (1) and hence doping Mn in  $\text{CaSO}_4$  has been found to be quite difficult. Mn gets easily oxidized to MnO. during doping process at high temperatures. In contrast, Mn could be doped easily in  $(\text{Ca},\text{Zn})\text{SO}_4$  or  $\text{Zn}_2\text{SiO}_4:\text{Mn}$ . since Zn has a higher EN (1.7) than that of Mn (1.6). This phosphor has double peak structure, one at  $130^\circ\text{C}$  and the other at  $240^\circ\text{C}$  whereas  $\text{CaSO}_4:\text{Mn}$  has a single peak at  $130^\circ\text{C}$ . At higher Mn concentrations it exhibits a single peak at  $240^\circ\text{C}$ . Its TL sensitivity is higher that of  $\text{CaSO}_4:\text{Dy}$  [6].

Another noteworthy sulphate based phosphor developed by author's group at IGCAR is  $\text{CaSO}_4:\text{Ag},\text{Tm}(\text{Dy})$  which has a high temperature TL glow peak at  $400^\circ\text{C}$  with a sensitivity comparable to that of  $\text{CaSO}_4:\text{Dy}$ . Its TL sensitivity did not vary with irradiation temperature in the range 100K to 520K and hence is ideal for radiation dosimetry at elevated temperatures such as in reactor cores etc [7].

## 2.2 Studies on Luminescence Mechanism

The aliovalent  $\text{Dy}^{3+}$  situating at  $\text{Ca}^{2+}$  site would create cation vacancies which help in stabilizing the hole traps giving rise to the TL peak near  $230^\circ\text{C}$  which is used in radiation dosimetry. This view is confirmed from the observation that in  $\text{CaSO}_4:\text{Dy}^{3+},\text{Na}^+$  the  $230^\circ\text{C}$  TL peak is absent. It exhibits a major TL peak near  $120^\circ\text{C}$  similar to the case with  $\text{CaSO}_4:\text{Mn}^{2+}$ . Despite intense studies based on ESR, the electron and hole traps giving rise to the  $230^\circ\text{C}$  peak in  $\text{CaSO}_4:\text{Dy}$  has not yet been identified without ambiguity. In contrast ESR studies in  $\text{CaSO}_4:\text{Ag}^+,\text{Dy}^{3+}$  have shown that on irradiation [8], thanks to the expertise of Dr. Gundu Rao from IIT, Mumbai,  $\text{Ag}^+$  acts as the hole trap (i.e  $\text{Ag}^+ \rightarrow \text{Ag}^{2+} + e^-$ ) while  $\text{SO}_3^-$  species formed by radiolysis of  $\text{SO}_4^{2-}$  (i.e  $\text{SO}_4^{2-} \rightarrow \text{SO}_3^- + \text{O}^-$ ) acts as electron traps (i.e  $\text{SO}_3^- + e^- \rightarrow \text{SO}_3^{2-}$ ). Thermal annealing and dose dependence studies of the ESR signals from paramagnetic  $\text{Ag}^{2+}$  and  $\text{SO}_3^-$  species confirmed the above correlation. Recombination of  $\text{O}^-$  with  $\text{SO}_3^-$  species takes place at higher temperatures ( $\sim 500^\circ\text{C}$ ).

Our recent studies have, however, thrown some insight into the defects causing TL in  $\text{CaSO}_4:\text{Dy}$  [9]. These studies revealed that  $\text{CaSO}_4:\text{Dy}$  prepared with  $\text{ZnSO}_4$  flux by solid state reactions at  $750^\circ\text{C}$  exhibit a high TL sensitivity. Its TL peak, however, occurs at  $120^\circ\text{C}$ . This was attributed to the presence of  $\text{O}_{2i}^{2-}$  (or  $\text{O}^- + \text{O}^-$ ) interstitial ions formed as a result of thermal dissociation of  $\text{ZnSO}_4$  at  $750^\circ\text{C}$  which result in the elimination of cation vacancies created by the presence of  $\text{Dy}^{3+}$  at  $\text{Ca}^{2+}$  sites. Charge transfer from oxygen interstitial ions to  $\text{F}^+$  centres (anion vacancies created by the presence of oxygen interstitial ions) occur during X-irradiation and a reverse of this process occur during TL readout giving

rise to  $120^\circ\text{C}$  TL peak. Zn perhaps exists as  $\text{Zn}^0$  atoms at interstitial sites. A similar process is envisaged in  $\text{CaSO}_4:\text{Mn}$ , the oxygen interstitials in this case perhaps arises from thermal oxidation of  $\text{MnSO}_4$ . In this case Mn should exist as  $\text{Mn}^{2+}$  at  $\text{Ca}^{2+}$  sites.

The above model can be extended to explain the TL process of  $230^\circ\text{C}$  peak in  $\text{CaSO}_4:\text{Dy}$ . Presence of  $\text{Dy}^{3+}$  at  $\text{Ca}^{2+}$  sites create cation vacancies. Anion vacancies ( $\text{F}^+$  centres) are created by the presence of oxygen interstitial ions created by thermal dissociation of Dysprosium sulphate. These interstitial ions act as hole traps while the  $\text{F}^+$  centres act as electron traps. In the vicinity of cation vacancies, the hole traps are more stable and hence the TL peak in this case occurs at a higher temperature ( $230^\circ\text{C}$ ). An advantage of this model is its ability to explain easily the anomalous result, namely a slow decline in TL sensitivity of  $\text{CaSO}_4:\text{Dy}$  on prolonged annealing at  $400^\circ\text{C}$  and subsequent recovery on  $700^\circ\text{C}$  anneal. No change in TL sensitivity was seen on annealing below  $400^\circ\text{C}$ . As per the above model, the  $400^\circ\text{C}$  anneal could thermally migrate slowly  $\text{O}_i^{2-}$  ions to  $\text{F}^+$  centres, thereby depriving electron and hole traps resulting in a loss in TL sensitivity and  $700^\circ\text{C}$  anneal could move the  $\text{O}_i^{2-}$  ions to their original sites thereby restoring the TL sensitivity. Thermal migration energy at  $300^\circ\text{C}$  is perhaps insufficient to displace  $\text{O}_i^{2-}$  ions from their original sites and hence no change in TL sensitivity is seen.

## 3. OUTSTANDING ISSUES

One of the outstanding issue, in my opinion, is the development of a TLD for high level radiation doses (from 30 Gy up to  $10^4 - 10^5$  Gy) used in food irradiation, sterilization and other radiation processing applications. Presently used TLDs either saturate or decline in their sensitivity at such high doses. The supralinear response in the intermediate dose region ( $10 - 10^3$  Gy) exhibited by some TLDs is also an issue. Ideally the TL response should increase uniformly (not necessarily linearly) over a wide dose range without saturation in a predictable and reproducible manner so that unknown radiation doses can be estimated easily using mathematical curve fitting. While supralinear TL response is attributed to the competing trap saturation during irradiation with progressive dose (eg.,  $\text{CaSO}_4:\text{Dy}$ ) or secondary electron track interaction during irradiation in the medium dose region (eg,  $\text{LiF}:\text{Mg},\text{Ti}$ ), saturation and decline in response at higher doses are attributed to limited number of traps and trap damage or trap conversion.

Recently, some reports suggest that nano phosphors exhibit linear response. Specifically,  $\text{CaSO}_4:\text{Dy}$  made by recrystallization when ground in a mortar and pestle to submicron sizes (top-down approach) for several hours is reported to exhibit a linear TL response in the dose range  $10^2$  Gy –  $6 \times 10^3$  Gy. A decline in TL sensitivity is, however, seen at  $7 \times 10^3$  Gy. Such a heavy grinding

reduces the TL sensitivity considerably which explains the high starting dose of  $10^2$  Gy. But the reason for the dose linearity up to  $6 \times 10^3$  Gy and the sudden decline at  $7 \times 10^3$  is not known. Moreover the dose-range covered in this study is too small for applications [10]. The bulk phosphor (~75 micron) also shows a near linear response in this narrow dose region [11]. Since the dose-response characteristics vary from batch to batch, a comparative study of bulk and finely ground  $\text{CaSO}_4\text{Dy}$  in the above dose range is essential before a definitive conclusion is drawn. One could use a neutral density filter to attenuate the TL signal from bulk phosphor to avoid instrument saturation in such studies. When several colleagues asked for an explanation of the above result at the ICLA-2015 conference in Bangalore, my answer was “reason unknown”, since no existing theory would explain a differential dose-response with grain size. More experimental results are needed before a conclusion can be drawn.

BRNS has sanctioned us a project to develop a linear and stable radiation dosimeter in the high dose region. We concentrated on radiophotoluminescence (RPL) of  $\text{F}_2$  and  $\text{F}_3^+$  centres in undoped LiF as well as TL in undoped LiF and  $\text{BaSO}_4$  and  $\text{SrSO}_4$ . These F-aggregate centres in LiF are created by radiolysis process due to the migration of fluorine atoms to dislocation sites during irradiation at room temperature. RPL has the advantage of repeated measurements since the luminescent centres are not destroyed during PL measurements unlike in TL. A commercial (Sunna dosimeter from USA) system based on this technique already exists. Interesting results on RPL have been obtained by us with home made as well as commercial LiF materials. LiF pellets have also been made successfully. Undoped sulphate materials were chosen for TL studies because high sensitivity is not needed in the high dose region. In fact the light emitted had to be attenuated heavily with the help of a neutral density filter to avoid instrument saturation. The TL response of some LiF materials was found to be perfectly linear in the dose range  $60 - 1.5 \times 10^4$  Gy disproving the myth that only nano phosphors give linear TL response in

the high dose region. A most interesting result obtained with  $\text{BaSO}_4$  is the dependence of dose-response characteristics on sintering temperature.

#### 4. CONCLUSION

In short, the journey to the development of TLD badge and luminescence phosphor research in DAE has been a pleasant and memorable one.

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