Letters

On the energy storage of calcium tungstate phosphor

Calcium tungstate phosphors are widely studied and known for their practical utility as phosphors in fluorescent lamps, scintillation counters, laser host materials and X-ray screens [1–6]. Because of this, the study of the luminescent properties of this material has been the subject matter of numerous scientific investigations for a long time. Much of the earlier work on such properties of these phosphors has been done under ultraviolet irradiation and not much attention has so far been given on the afterglow and the energy storage properties of this material; these aspects of study are of interest since most of the efficient phosphors are expected to exhibit, apart from other features, minimum afterglow and thermoluminescence. Keeping this in mind, the afterglow decay and thermoluminescence (TL) of calcium tungstate phosphors prepared in our laboratory have been studied under X-ray irradiation at room temperature (25° C).

Calcium tungstate phosphors are prepared by using Analar grade starting materials ($CaCO_3$ and tungstic acid) which are easily available in the country. $CaCO_3$ (BDH Analar) and tungstic acid (E. Merck) in the molar ratio 1:1 are mixed and ground thoroughly in a pulverizer. A yellow slurry mass is formed with the addition of appropriate quantity of distilled water. The mass becomes white when dry. This is then dired further in an air oven at 100° C for about 8 h so that the resultant mass becomes as white as possible. After being ground the white mass is transferred to a platinum crucible and fired in air at about 1000° C for about 1 h depending upon the quantity of the starting material. The material is thoroughly ground and sieved through 54 μm mesh, taking all the essential precautionary measures to avoid contamination before, during and after firing. In all the measurements the material is used at different times without further heat-treatment.

In all cases the phosphor is tightly packed in a brass sample-well and exposed to X-rays (Cu target, 30 kV, 10 mA) at room temperature for about 8 min. The block diagram of the apparatus designed and constructed by us in the laboratory is shown in Fig. 1. After excitation, the sample-well is rigidly fixed to a sample holder inside a vacuum chamber (10^{-3} Torr) and the light emitted by the phorphor before heating as well as under a constant heating rate (28 ± 1° C $\min^{-1}$), is recorded using an RCA 1P28 photomultiplier tube as the detecting device in conjunction with an ECIL EA 812 electrometer amplifier and two millivolt recorders.

The phosphorescence decay from the samples could be recorded only after 8 min X-ray irradiation since this length of time has generally elapsed in transferring the samples and evacuating the vacuum chamber. Immediately after the afterglow decay is recorded, the energy still stored by the sample is estimated by recording the emission when the samples are heated to 400° C under a constant rate of heating. The temperature of the sample during heating is measured using a Cu–constantan thermocouple.

Several samples of $CaWO_4$ were studied: even after repeated cycles of irradiation and heating they were found to exhibit reproducible patterns emitting a very weak long-period afterglow and

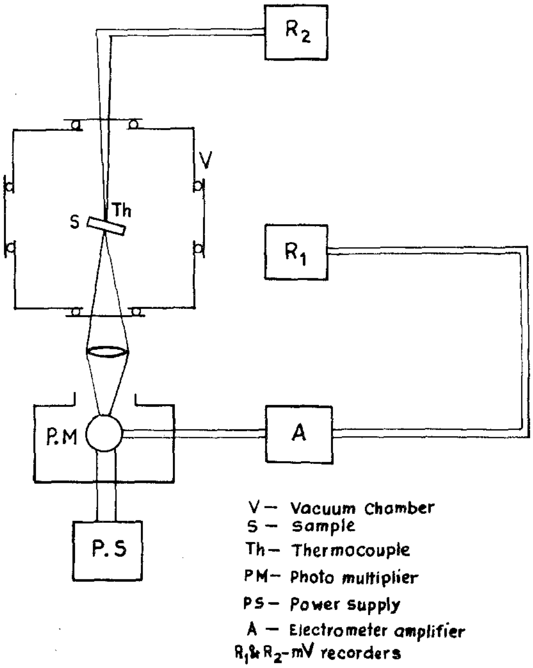

Figure 1 Schematic drawing of the apparatus.

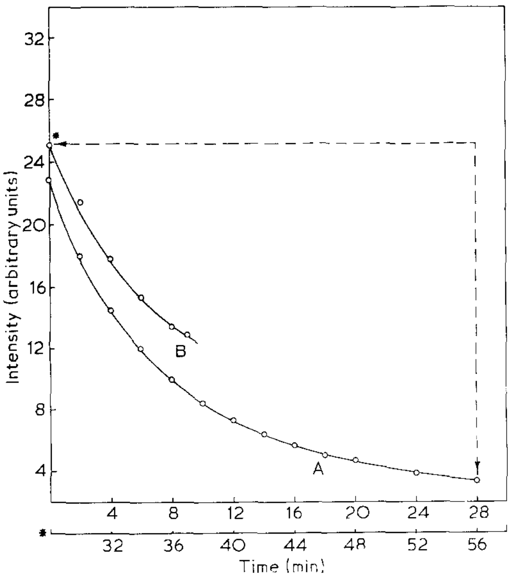

Figure 2 Afterglow decay of $CaWO_4$ irradiated by 30 kV, 10 mA X-rays at room temperature (25° C). (A) 8 min after irradiation (B) 35 min after irradiation.

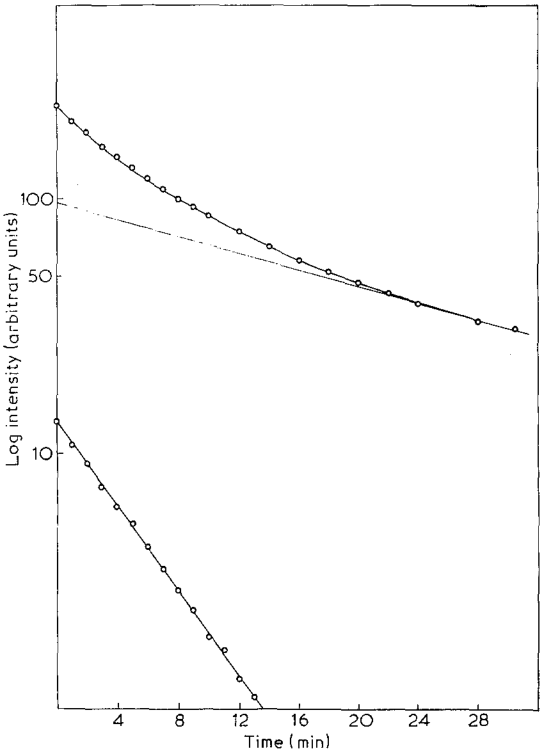

Figure 3 Analysis of the decay curve shown in Fig. 2.

thermoluminescence which could be measured with good precision by operating the amplifier in its sensitive range. The afterglow decay measured at room temperature for one sample is shown in Fig. 2; this figure also shows the very feeble and persistant afterglow emitted by the sample about 40 min after exposure (curve B). It is observed, generally that the intensity of afterglow decays at different stages following an exponential law, and thus the entire decay curve is analysed using the expression $I = \Sigma_i I_i \exp(-\alpha_i t)$, where I_i is the afterglow intensity and α_i the decay constant at the corresponding stage. The results of such an analysis are shown in Fig. 3.

Fig. 4 shows the glow curves recorded for samples stored in the dark after irradiation for different lengths of time; the heating rate in all these cases is maintained at 28 ± 1° C. The thermoluminescence glow curves exhibited a single glow peak with a glow maximum $T_m = 361$ K and half-width $W = 36.5$ K, which are found to remain practically unchanged with storage time. Further, no thermoluminescent emission is observed from the samples if they are stored longer than 12 h after irradiation.

The glow curves are analysed applying first order kinetics; the trap depth, E, and the frequency factor, S, are calculated using Chen's formula [7] $E = 2.29 KT_m^2/W$ and $S = 2.67 (\beta/W)\, 10^{T_m/W}$ where β is the rate of heating. The value of the trap depth calculated as above is also compared with that obtained by using the initial rise method [8]. For this purpose the intensity of the rising portion of the glow curve is recorded by operating the photomultiplier at a higher voltage and the electrometer amplifier in the higher sensitive range; the results for one case are shown as an inset in Fig. 4. Utilizing the same value of the frequency factor obtained from the glow curve analysis, the E values are also calculated for the traps observed in the afterglow decay (Fig. 3) for the two stages; all these values are presented for comparison in Table I.

Calcium tungstate in the form of powders as well as single crystals are well known phosphors having a Scheelite crystal structure and representing the class of self-activated luminescent materials emitting blue fluorescence in the broad region between 360 and 600 nm with a peak around 440 nm under untraviolet, electron, X-ray and other ionizing radiation. In the present study it

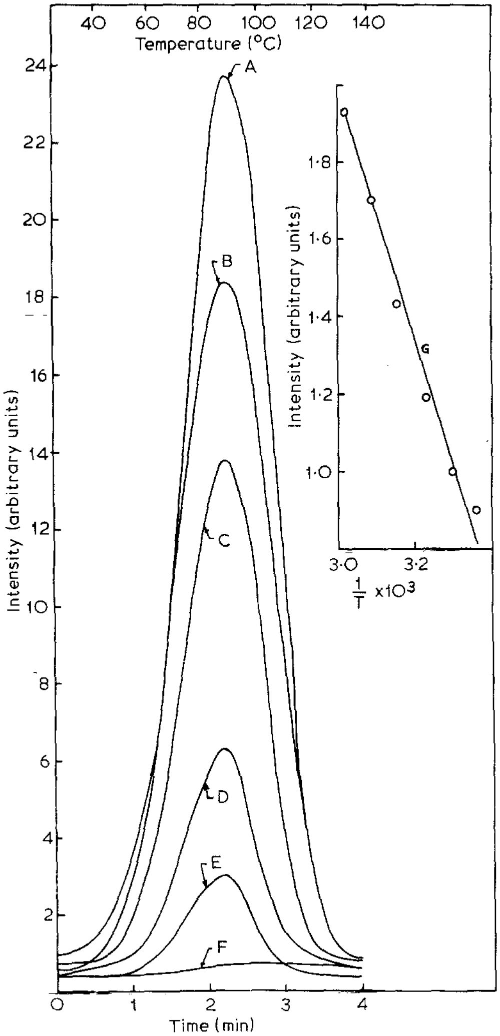

Figure 4 Thermoluminescence glow curves of CaWO$_4$ irradiated by X-rays (Cu target, 30 kV, 10 mA) at room temperature. The glow curves are recorded after different storage times in darkness, after (A) 30 min, (B) 2½h, (C) 4½h, (D) 6½h, (E) 8½h, (F) 12½h. Inset: the initial rise plot of one of the glow curves.

has also been observed that the thermoluminescent emission seen by the naked eye is found to be light blue in colour similar to that observed in the X-ray fluorescence during irradiation. Tready and Powell [9] also report blue fluorescence under ultraviolet excitation.

TABLE I Values of the trapping parameters

Serial no.	Method	Trap depth E (eV)	Fequency factor S (sec^{-1})
(1)	Thermoluminescence glow curve	0.70	2.66×10^8
(2)	Afterglow decay 2nd stage	0.69	2.66×10^8
(3)	Afterglow decay 1st stage	0.64	2.66×10^8
(4)	Initial rise	0.66	4.47×10^7

Since the first order kinetics and the exponential law are suitable for analysis of the thermoluminescence glow curve and the afterglow decay respectively, the structural or impurity defects likely to be produced in the phosphor during excitation might have been distributed in the region around the tungstate (WO_4^{2-}) ion. It may also be speculated that due to the presence of these trapping states, the S_4 summetry of the WO_4^{2-} ion will be perturbed, resulting in the storage of excitation energy in one of the (metastable?) states associated with the T_1 levels of the tungstate ion. The fact that these traps are found to be destroyed during heating as well as during storage at room temperature in a monomolecular radiative recombination process, also supports this theory.

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Growth of polycrystalline diamond

Polycrystalline diamond is currently under intense investigation for its application to cutting tools [1]. Natural polycrystalline diamonds such as ballas and carbonado are rarer forms of diamond found only at a limited number of mines. Synthesis of polycrystalline diamond is, therefore, interesting both from the engineering stand point and for the study of the origin of natural polycrystalline diamond.

Ballas is a form of diamond with globular shape in which the crystallites are arranged radially. It has probably grown from its centre to the surface [2]. Ballas-like diamond was synthesized by Kalashnikov *et al.* [3]. The synthesizing condition, however, was not described.

Carbonado is an aggregate of randomly oriented small diamond crystals [4] and carbonado-type diamond has been prepared by sintering and other methods [5–8].

In this letter we report on the growth features of polycrystalline diamond formed under high pressure and high temperature in the presence of group VIII metals, especially cobalt. Shock-synthesized diamond powder (0 to 2 μm grade obtained from DuPont Co Ltd) was used as the starting material. Natural and catalytically synthesized diamond powder of different sources and particle size distribution were also tried, but no distinct tendency to agglomeration or growth of diamond particles was observed.

High temperature and pressure experiments were carried out using a belt apparatus. The sample assembly is shown schematically in Fig. 1a. The diamond powder was charged around a rod of a catalyst metal placed at the centre of the cell. In all runs pressure was first applied and then temperature. The samples were maintained at 70 kbar and 1600° C for 5 min. Temperature was then lowered by turning off the electric power to the heater before releasing the pressure.

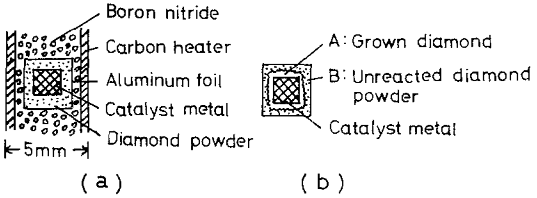

Figure 1 Sample assembly (a) before and (b) after high temperature and pressure experiments.

After the run the appearance of the sample portion was changed as shown in Fig. 1b. The diamond specimens were observed to be distinctly separated into two layers, A and B (Fig. 1b). Using X-ray diffraction, the inner layer A was found to consist of diamond and the catalyst metal. Growth and agglomeration of crystals were observed in this layer as will be described below. No significant change was observed in the outer layer B except for partial graphitization.

The growth features were examined by scanning electron microscopy (SEM). The catalyst metal in the specimens was removed by a hot mixture of HNO_3 and HCl prior to SEM observation. Figs. 2 to 5 show typical growth features of the inner layer A, obtained from the system of the shock-synthesized diamond and cobalt.

The reacted layer A of about 0.2 mm thick was again separated into three zones C, D and E by its texture. The cross-sectional view of the reacted region is shown in Fig. 2. Zone C is the boundary with the catalyst metal and zone E the outermost zone of the reacted diamond layer.

The grown single crystals having a definite shape and form were observed at the zone C. The zone D consisted of loosely packed aggregates of diamond of about 1 μm as shown in Fig. 3. The orientation of the crystals in this region was random. Some of the crystals showed the same well-defined morphology as that of single crystals. Agglomeration