Photoconductivity studies of (PbCrO$_4$-HgO-ZnO) composites

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Abstract. This paper deals with the photoconductivity studies of (PbCrO$_4$-HgO-ZnO)
composites comprising of base materials of three different energy gaps. The response of
(10% PbCrO$_4$-80% HgO-10% ZnO) and (20% PbCrO$_4$-60% HgO-20% ZnO) composites is
faster than that of other compositions and of base materials. The dark current for (20% PbCrO$_4$-
60% HgO-20% ZnO) is trap limited-space charge limited at higher voltages while it shows
non-ohmic behaviour at lower voltages. The photocurrent for (20% PbCrO$_4$-60% HgO-
20% ZnO) composition shows non-ohmic behaviour at lower voltages and tends to saturation
at higher voltages. The photocurrent for the above composition varies sublinearly with the
intensity of illumination. The (10% PbCrO$_4$-80% HgO-10% ZnO) composition is the best
suitable material for optical switching. The existence of discrete trap depths at 16°C appears
plausible for different compositions.

Keywords. Dielectric; photosensitive; photoconductors.

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1. Introduction

It is well known that the rise and decay curves of photocurrent are governed by the
trapping states and recombination centres lying in the forbidden zone of a
photoconductor. Therefore these curves can be used to understand the nature and
distribution of traps and recombination centres. A good photosensitive material
should not only show a large change in conductivity but also respond fast. If trapping
centres are in abundance, the response time is slow. Trapping also increases the decay
time, as the carriers are slowly released after removal of the excitation source. The
increased carrier concentration in presence of light is a function of intensity of
illumination, temperature, applied field and various other parameters [1]. The nature
of current versus intensity curve gives an idea about the charge trapping and
recombination processes taking place inside the material.

Photoconducting properties of a large number of single crystals have been studied.
Thick and thin layers have also been investigated by several workers [2–6]. However
relatively fewer attempts have been made for mixed binder layers. In the present
investigations, the three base materials i.e. PbCrO$_4$, HgO, ZnO having different band
gaps of values 2·3 eV, 0·3 eV and 3·2 eV respectively have been mixed in different
proportion by weight in order to use the effect of composition and synthesizing
conditions on photoconducting properties of mixed systems.

2. Experimental

The ($PbCrO_4$-HgO-ZnO) mixed lattices having different compositions were prepared by the usual technique. High purity base materials i.e. $PbCrO_4$, HgO, ZnO were mixed in different proportion by weight and ground for homogeneous mixing. The mixtures were fired at 400°C in a cylindrical furnace in air atmosphere for 40 min.

The finely powdered microcrystalline fired samples were added to polystyrene binder in benzene and sandwiched between two conducting surfaces of two glass plates. One of the surfaces of the glass plate was made conducting by spreading a layer of SnO_2 over it. The conducting layers of glass plates were kept in contact with the sandwiched binder layer. Thick binder layers were deposited on an area of about $3 cm^2$ having thickness varying from 0·025 cm to 0·073 cm. Measurements were made with these parallel plate capacitors due to ease and economy of process.

The cell was connected to a nanoammeter (model NM-122, Scientific Equipment, Roorkee) and d.c. power supply in series and kept in a dark metallic box. The box consists of a hole on its upper surface and the cell was kept below the hole. Upper surface of the cell could be illuminated with radiations from a Hg-lamp. Intensity of illumination was varied by varying the slit width and the intensity over the cell surface was measured using a Luxmeter.

3. Results and discussion

Mixed systems having different proportions of base materials were prepared for comparative study. These are (20% $PbCrO_4$-60% HgO-20% ZnO), (60% $PbCrO_4$-20% HgO-20% ZnO), (20% $PbCrO_4$-20% HgO-60% ZnO) and (10% $PbCrO_4$-80% HgO -10% ZnO) apart from base materials. Photoconducting properties of these systems have been studied in order to obtain optimum conditions of photoresponse and to find possible use of the layers in many fields i.e. in light switching circuits, photo-conductor photocells, electrophotography, pickup tube, light amplifiers etc. The results are as follows:

3.1 *Rise and decay of photocurrent*

The rise and decay of photocurrent for different compositions under white light is shown in figure 1. The photosensitivity of (10% $PbCrO_4$-80% HgO-10% ZnO) composition is more than the other mixed systems except pure HgO under experimental conditions. The response of (10% $PbCrO_4$-80% HgO-10% ZnO) and (20% $PbCrO_4$-60% HgO-20% ZnO) compositions is found to be fastest under experimental conditions. The response time for all compositions is listed in table 1, where response time is defined as the time required by the photocurrent to take 90 per cent of its maximum value. For 100% HgO, photocurrent continues to increase i.e. only positive photoconductivity results. Positive photoconductivity is defined as the increase in conductivity in presence of light. For (10% $PbCrO_4$-80% HgO-10% ZnO), 100% $PbCrO_4$, (20% $PbCrO_4$-60% HgO-20% ZnO), (20% $PbCrO_4$-20% HgO-60% ZnO) and (60% $PbCrO_4$-20% HgO-20% ZnO) compositions, the photocurrent rises as soon as the light is switched on but after acquiring a maximum value, it continues to decay for a very long time tending towards a saturation value i.e. both positive and negative photoconductivity results, where negative photoconductivity [7] is defined as the decrease in conductivity in presence of light. For (60% $PbCrO_4$-20% HgO-20% ZnO)
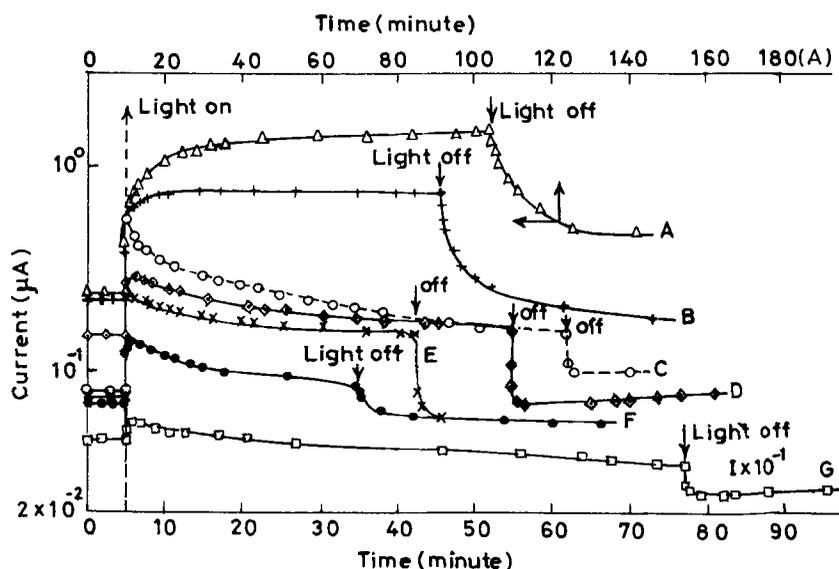
Figure 1. Rise and decay of photocurrent in layers having different compositions. A, B, C, D, E, F and G for 100% HgO, 100% ZnO, (10% $PbCrO_4$-80% HgO-10% ZnO), (60% $PbCrO_4$-20% HgO-20% ZnO), (20% $PbCrO_4$-60% HgO-20% ZnO), 100% $PbCrO_4$ and (20% $PbCrO_4$-20% HgO-60% ZnO) systems respectively; field = 81·6 V/cm, room temperature = 20·5°C and intensity of illumination = 2000 lux.

Table 1. Response time of photocurrent.

Composition	Response time (sec)
10% $PbCrO_4$-80% HgO-10% ZnO	2
20% $PbCrO_4$-60% HgO-20% ZnO	2
60% $PbCrO_4$-20% HgO-20% ZnO	9
20% $PbCrO_4$-20% HgO-60% ZnO	9
100% $PbCrO_4$	8
100% HgO	3360
100% ZnO	258

composition, positive photoconductivity is almost equal to the negative photoconductivity. For (20% $PbCrO_4$-20% HgO-60% ZnO) sample, negative photoconductivity becomes greater than the positive photoconductivity. However, for 100% $PbCrO_4$, (20% $PbCrO_4$-60% HgO-20% ZnO) and (10% $PbCrO_4$-80% HgO-10% ZnO) compositions, the positive photoconductivity is greater than the negative photoconductivity. For 100% ZnO sample, negative photoconductivity may be neglected in comparison to the positive photoconductivity.

When illumination of the photoconductor increases the density of electrons or holes or both, positive photoconductivity results. If with the elapse of time, the minority carriers are also excited from the imperfection centres, a negative photoconductivity results. This is due to the rapid recombination of minority carriers

with majority carriers. This explains why negative photoconductivity results with positive photoconductivity.

The response of (10% $PbCrO_4$-80% HgO-10% ZnO) and (20% $PbCrO_4$-60% HgO-20% ZnO) compositions is the fastest in comparison to the other compositions but the photocurrent for (10% $PbCrO_4$-80% HgO-10% ZnO) composition remains at its maximum value for a short while and then continues to decay rapidly under experimental conditions. However, the photo current for (20% $PbCrO_4$-60% HgO-20% ZnO) composition remains at its maximum value for a comparatively longer time before its decay. So, the general measurements i.e. effect of field, intensity of illumination etc. have been made for (20% $PbCrO_4$-60% HgO-20% ZnO) composition.

3.2 *Transient effect*

Photocurrent for mixed systems increases as soon as the light is switched on and after acquiring a maximum value, it begins to decay for a very long time even in the presence of light. When the light is switched off, the current takes a long time to reach its dark level or sometimes it goes below the dark level (figure 1). Now if the light is switched off before the decay of photocurrent starts, the current decays rapidly to reach its dark level (figure 2). Such type of studies have been carried out to explore the possible use of layers in switching circuits. The response of (10% $PbCrO_4$-80% HgO-10% ZnO) and (20% $PbCrO_4$-60% HgO-20% ZnO) compositions is very quick in comparison to other composites. As soon as the light is switched off, the (10% $PbCrO_4$-80% HgO-10% ZnO) composition acquires its dark level quickly in comparison to the other compositions. Thus the (10% $PbCrO_4$-80% HgO-10% ZnO) is best for optical switching.

The decay curves of photocurrent for the above compositions have been used to calculate the trap depths. The decay of photocurrents after the cessation of excitation is given in figure 3. Photocurrent (I_p) has been obtained by subtracting the dark
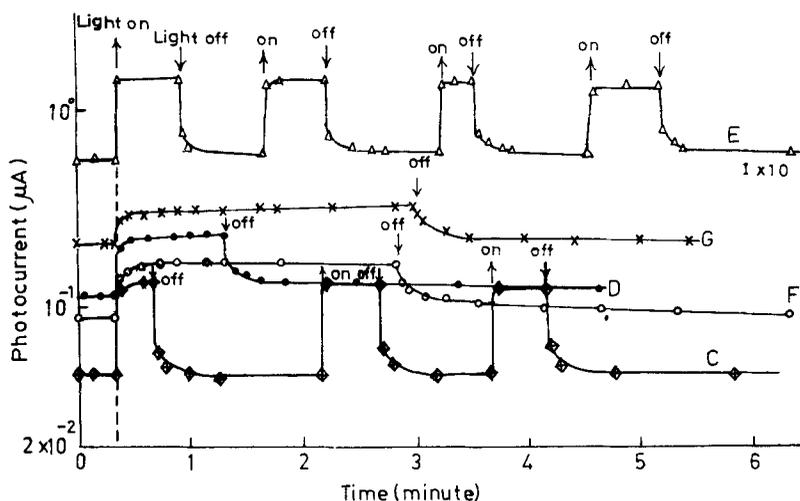

Figure 2. Rise and decay of photocurrent for different compositions. C, F, D, G and E for (10% $PbCrO_4$-80% HgO-10% ZnO), 100% $PbCrO_4$, (60% $PbCrO_4$-20% HgO-20% ZnO), (20% $PbCrO_4$-20% HgO-60% ZnO) and (20% $PbCrO_4$-60% HgO-20% ZnO) respectively; field = 81·6 V/cm; intensity = 1000 lux and room temperature = 16°C.
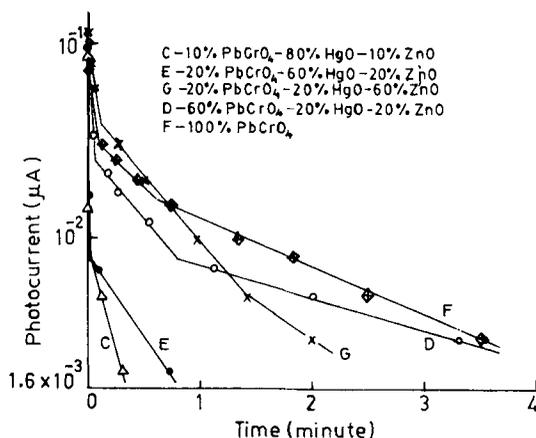
Figure 3. Decay of photocurrent for different compositions; field $= 81\cdot 6$ V/cm; intensity $= 1000$ lux and room temperature $= 16°$C.

Table 2. Calculated p-values for different compositions.

Composition	$p \times 10^3$		
	First exponential	Second exponential	Third exponential
10% PbCrO$_4$-80% HgO-10% ZnO	867	76·4	—
20% PbCrO$_4$-60% HgO-20% ZnO	822	33·0	—
60% PbCrO$_4$-20% HgO-20% ZnO	309	27·3	6·55
20% PbCrO$_4$-20% HgO-60% ZnO	162·6	26·8	11·9
100% PbCrO$_4$	201	22·1	9·71

current from the total current. The plots of log I_p versus time for decay mode show that decay cannot be governed by a single exponential law. This implies that the traps of different nature are situated at different energy depths below the lower edge of the conduction band.

Thus, the decay is given by the relation,

$$I = I_0 \exp(-pt), \tag{1}$$

where p is the probability of escape of an electron from the trap per second and its value is different for different straight line sections, I_0 is the current at the moment light is interrupted and I is the current at any instant of time. The calculated p-values (slopes of the straight lines) are listed in table 2.

The probability of an electron escaping from a trap is also given by the relation

$$p = S \exp(-E/kT), \tag{2}$$

where k is the Boltzmann constant, T is the absolute temperature and S is the frequency factor, the "attempt to escape frequency". It is defined as the number per second that the quanta from crystal vibrations (phonons) attempt to eject the electrons from

the traps multiplied by the probability of transition from trap to the conduction band, and is of the order of 10^9.

The trap depths (E) corresponding to different exponentials are calculated using (1) and (2) and is given by

$$E = kT\left[\log_e S - \log_e\left(\frac{\log_e I_0/I}{t}\right)\right].\tag{3}$$

The calculated values of trap depths for different compositions are listed in table 3.

3.3 Field dependence

Dark current for (20% $PbCrO_4$-60% HgO-20% ZnO) composition begins to decay from its maximum value as soon as the voltage is switched on (figure 4). Dark current decays for a long time before acquiring a stable value. Measurements have been taken

Table 3. Trap ionization energies of different traps corresponding to different exponentials.

Composition	Trap depth (eV)		
	First exponential	Second exponential	Third exponential
10% $PbCrO_4$-80% HgO-10% ZnO	0·52	0·58	—
20% $PbCrO_4$-60% HgO-20% ZnO	0·52	0·6	—
60% $PbCrO_4$-20% HgO-20% ZnO	0·55	0·61	0·64
20% $PbCrO_4$-20% HgO-60% ZnO	0·56	0·61	0·63
100% $PbCrO_4$	0·56	0·61	0·63

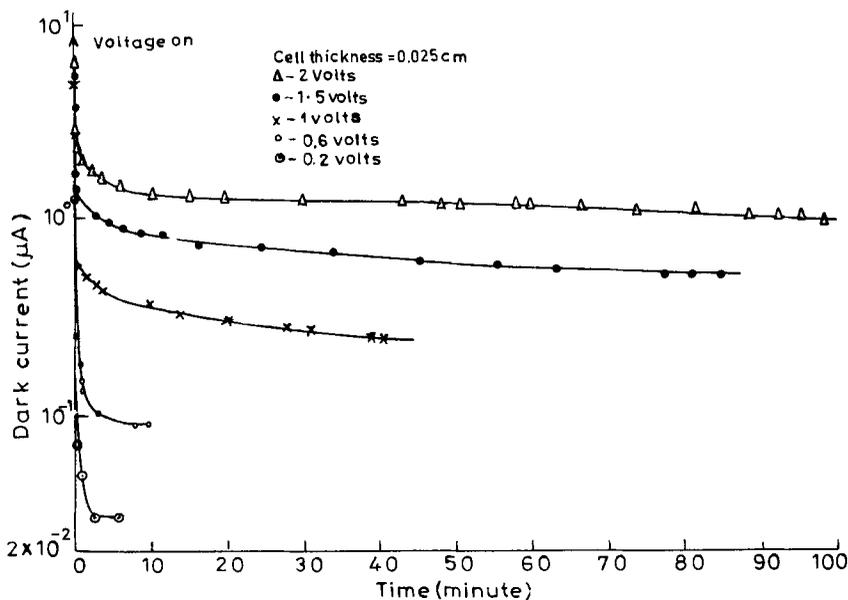**Figure 4.** Decay of dark current at different fields for (20% $PbCrO_4$-60% HgO-20% ZnO) composition; room temperature = 32·5°C.

at different voltages. Decay of dark current with time indicates the presence of large density of trapping states inside the material. As soon as the voltage is switched on, dark current acquired its maximum value due to the motion of charge carriers but with the elapse of time, carriers begin to trap in trapping levels. As time passes, more and more charge carriers are trapped, thereby decreasing the dark current with time. At saturation (stable value of current), an equilibrium is established when the number of electrons making transition to the trapping levels from conduction band becomes equal to the number of electrons making transition to the conduction band from trapping levels per second.

Rise and decay of photocurrent for (20% PbCrO₄-60% HgO-20% ZnO) composition at different voltages is shown in figure 5. Figures 4 and 5 have been used to obtain figure 6 which shows the variation of dark current and photocurrent with voltage. Photocurrent was obtained by subtracting the dark current from the total current. The curves are drawn on a log-log scale. The curves are straight lines having different slopes at different regions of the curve. Only the photocurrent tends to saturation at higher voltage range. Thus, the straight line sections may be represented by $I \propto V^r$ where I is the current and r is the slope of the straight line section.

Above 0·6 V the dark current varies with voltage according to an index greater than 2. Smith and Rose [8] interpreted these currents as space charge limited currents and such type of variation was attributed to the effect of traps. Therefore, these currents may be interpreted as trap limited as well as space charge limited currents [9]. The non-ohmic behaviour $(r > 1)$ of the photocurrent suggests that some carriers are being injected into the material. The photocurrent tends to saturation at high fields. This can be explained [4] on the basis of class-II states which are the imperfection centres lying in the forbidden gap just above the valence band. These class II centres have greater capture cross-section for holes than for electrons [10]. A dielectric material
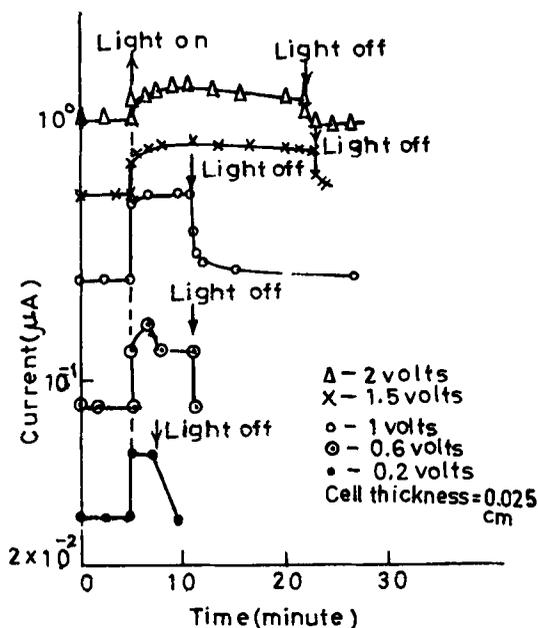

Figure 5. Rise and decay of photocurrent for (20% PbCrO₄-60% HgO-20% ZnO) composition at different fields; intensity = 5700 lux; room temperature = 32·5°C.
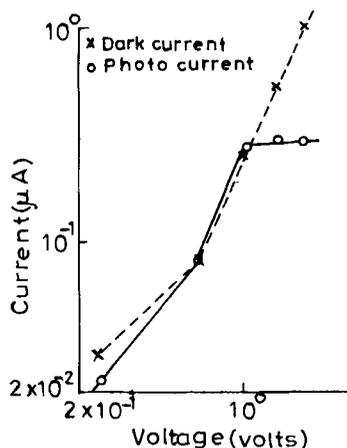
Figure 6. Variation of dark current and photocurrent with voltage for (20% PbCrO$_4$-60% HgO-20% ZnO) composition; intensity = 5700 lux; room temperature = 32·5°C.
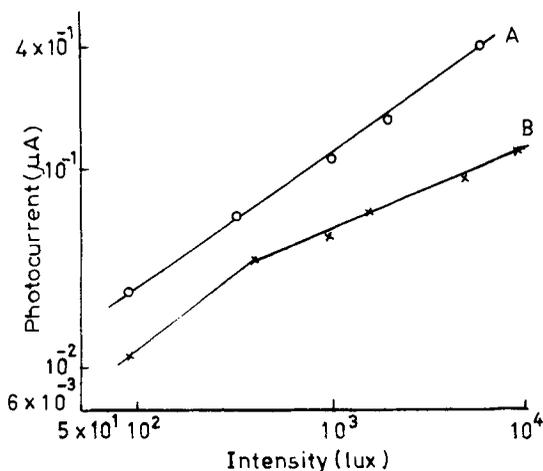

Figure 7. Variation of photocurrent with intensity of illumination for (20% PbCrO$_4$-60% HgO-20% ZnO) composition. A, at 30°C; B at 11°C and field = 40 V/cm.

has only one Fermi-level in the dark. But in the presence of light, there exists two Fermi-levels, one for electrons and another for holes. It may be assumed that at a particular light intensity and voltage the position of the Fermi-levels are such that they have just converted all the class-II states into recombination levels. An additional voltage causes the flow of more electrons into the material which raises the Fermi-level upwards towards the conduction band. Thus some of the class-II centres are converted into hole traps. This process desensitizes the sample and decreases electron life time with increasing voltage.

3.4 *Effect of intensity of illumination*

The variations of photocurrent with light intensity at two different temperatures are shown in figure 7 on a log-log scale. These are straight line curves. Thus the variation

can be represented by $I_p \propto L^r$. The value of r is < 1 for the whole region of intensity of illumination. This shows that photocurrent varies sublinearly with the intensity of illumination. This suggests a continuous trap distribution though exponential in nature below the lower edge of the conduction band. An increase in intensity would convert more of the trap levels to recombination levels thereby decreasing the electron lifetime and giving rise to observed sublinearity.

As the temperature is increased from 11°C to 30°C, photocurrent increases (figure 7) which suggests that the Fermi level is moving across an exponential trap distribution [7].

4. Conclusions

The response of $(10\% \, PbCrO_4\text{-}80\% \, HgO\text{-}10\% \, ZnO)$ and $(20\% \, PbCrO_4\text{-}60\% \, HgO\text{-}20\% \, ZnO)$ compositions is very quick. The existence of an exponential trap distribution below the lower edge of the conduction band and existence of sensitizing centres near the valence band are confirmed for $(20\% \, PbCrO_4\text{-}60\% \, HgO\text{-}20\% \, ZnO)$ composition. Dark current versus voltage curve for the $(20\% \, PbCrO_4\text{-}60\% \, HgO\text{-}20\% \, ZnO)$ composition, shows the flow of trap limited as well as space charge limited current inside the material at higher voltages. It is also concluded that the $(10\% \, PbCrO_4\text{-}80\% \, HgO\text{-}10\% \, ZnO)$ composite is best for optical switching. The existence of discrete trap depths appears plausible for different compositions.

Acknowledgement

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