Dielectric Changes in Inorganic Phosphors

Stanley Kronenberg and Carl A. Accardo

Signal Corps Engineering Laboratories, Fort Monmouth, New Jersey

(Received April 6, 1955)

Phosphors of the ZnS—CdS type under an applied ac field exhibit capacity changes when illuminated. The measurements indicate that in some phosphors the change in capacity may not be attributed solely to a change in ohmic resistance. A possible explanation for the mechanism involved in these cases is given. Capacity decay data and photoconductivity decay at room temperature and liquid nitrogen temperature are discussed. Voltage-dependence data at various frequencies are also included.

IT has been reported that a condensor in which a phosphor of the ZnS—CdS type is used as a dielectric changes capacity when exposed to light.[1-3] According to Garlick and Gibson a real change in dielectric constant occurs and the effect cannot be attributed to photoconductivity. This conclusion is supported by measurements on the ac conductivity in phosphorescent solids as a function of the incident light intensity. These authors observe a saturation in conductivity with increasing light intensity while in the dc measurements on photoconductivity saturation does not take place. A theory is proposed by these investigators whereby trapped electrons which experience large displacements in the applied field account for the dielectric change. In a later paper, Kallmann introduced an electrical model for a powdered phosphor (identical to the one used in this paper) and could explain his experimental results solely on the basis of photoconductivity within the grains of the phosphor.[4] In the present investigation experiments are described which indicate that in certain phosphors the observed capacity change may be attributed to both photoconductivity and a real increase of the dielectric constant.

The experimental arrangement is illustrated in Fig. 1. The phosphors, which were commercially obtained, are deposited between conductive glass plates (Nesa glass) and compressed in a Lucite holder.

In some experiments the effect of the conductive glass series resistance was reduced by coating the plates with a thin aluminum layer (5% transmission). In some samples the phosphor was mixed in an Acetone-Duco cement base. This was done in order to insulate the grains from each other, although the results obtained in this manner did not differ from those in which the phosphor was deposited dry. The sensitive area of the samples used in the experiments was 6.25 cm² with an average thickness of 0.1 mm. Bronze clamps served as electrical contacts to the glass plates. To insure uniform excitation through the phosphor the assembly was mounted between two mirrors oriented 45° with respect to the sample. The visible light of a tungsten lamp or

ultraviolet light from a mercury arc was used for excitation; an infrared lamp together with a filter (cutoff at 8500 A) served to quench the phosphor before each experiment. The capacity and dissipation factor measurements were performed with a General Radio 716-C Bridge. The voltage across the sample at balanced position was kept constant for each series of measurements.

The equivalent circuit of a microcrystalline powder may be approximated by the circuit shown in Fig. 2. C_A represents the capacity of the air space between grains; C_p and R are the capacity and photosensitive resistance of the solid matter. The complex impedance (Z) of this circuit is given by the expression

$$Z = \frac{1}{j\omega C_A} + \frac{R}{1 + j\omega C_p R}.$$

The measured value of the capacity (C) obtained with the bridge is given by ($2\pi f \times$ imaginary part of the complex impedance)$^{-1}$, where f is the frequency of the applied voltage. From this we obtain that

$$C = C_A \frac{1 + \omega^2 C_p^2 R^2}{\omega^2 R^2 (C_A + C_p) C_p + 1}.$$

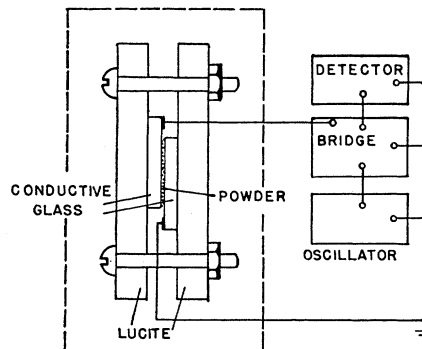The dissipation factor D for the circuit is given by the

FIG. 1. Experimental arrangement used for measurements of capacity and dissipation factor *versus* frequency. In some cases a thin sheet of mica was placed between the powder and the conductive side of the glass plate.

[1] P. Lenard and S. Saeland, Ann. phys. **28**, 240 (1909).
[2] F. Goos, Ann. phys. **34**, 77 (1939).
[3] G. F. J. Garlick and A. F. Gibson, Proc. Roy. Soc. (London) **60**, 574 (1948).
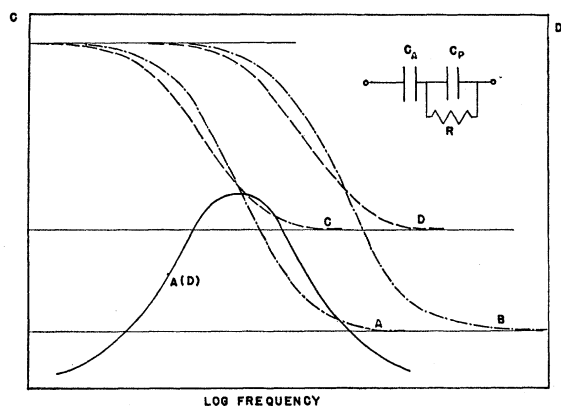[4] Kallmann, Kramer, and Perlmutter, Phys. Rev. **89**, 700 (1953).

FIG. 2. Capacity characteristics of the electrical model which represent the sample. A is the basic curve. A decrease in resistance shifts this curve to B; higher C_p shifts it into position C. Curve D is obtained when both changes take place. $A(D)$ shows the dissipation factor for curve A.

real part of Z divided by imaginary part of Z, or

$$D = \frac{R\omega C_A}{R^2\omega^2 C_p(C_p+C_A)+1}.$$

For low frequencies provided that $(\omega C_p)^{-1}\gg R$, C becomes equal to C_A; for high frequencies provided $(\omega C_p)^{-1}\ll R$ the equation for C becomes

$$C_A C_p/(C_A+C_p).$$

The dependence of C on frequency for constant values of R and C_p is shown in curve A of Fig. 2. For smaller values of R (C_p held constant) the curve shifts to higher frequencies (curve B). For the case in which C_p (R held constant) increases one obtains curve C in Fig. 2. Both a decrease in R and an increase in C_p results in Curve D. The corresponding $D(\omega)$ curves peak at the frequency where

$$C=\tfrac{1}{2}[C_A-C_A C_p/(C_A+C_p)]$$

The frequency dependence of C for variable light intensity has been measured for several phosphors at room and liquid nitrogen temperature. The data at 25°C for two typical powders is illustrated in Figs. 3(a) and 4(a). From Fig. 3(a), it is seen that the curves

TABLE I. Characteristics of some representative powders.

Powder	Fluorescence	Persistence	Components and activators
Powders showing photoconductivity and dielectric effect			
DuPont 1619	white	medium short	ZnS, CdS, Ag
DuPont 1800	orange	short	ZnS, CdS, Cu, Ag
RCA F2039	red	short	ZnS, CdS, Ag
RCA F2030	blue	long	ZnS, Ag
Powders which do not show dielectric effect			
DuPont 1301	yellow orange	long	ZnS, CdS, Cu, Ag, Fe
DuPont 1300	green	very long	ZnS, Cu, Ag, Ni, Fe

for Dupont 1301 powder in darkness and under illumination behave similar to curves A and B of Fig. 2; at high frequencies the capacity of the sample under illumination approaches the dark value:

$$C_A C_p/(C_A+C_p).$$

Thus we may conclude that in this powder the photoconductivity (ohmic resistance change within the grains) accounts for the measured capacity change. This is in agreement with the measurements of Kallmann *et al.* for this powder. The curves for powder 1619 under illumination, on the other hand, become parallel at high frequencies to the dark capacity curve. This behavior is similar to curve D in Fig. 2. Similar results for other powders appear to indicate that the phosphors may be divided into two general classes; those where the capacity change may be explained solely by photoconductivity and those where this is not the case. Table I lists a few representative powders which show the effect. It is seen that the $D(\omega)$ curves [Figs. 3(b) and 4(b)] have a similar shape to that predicted by the formula for D. As the grains are not distributed uniformly within the sample, a better
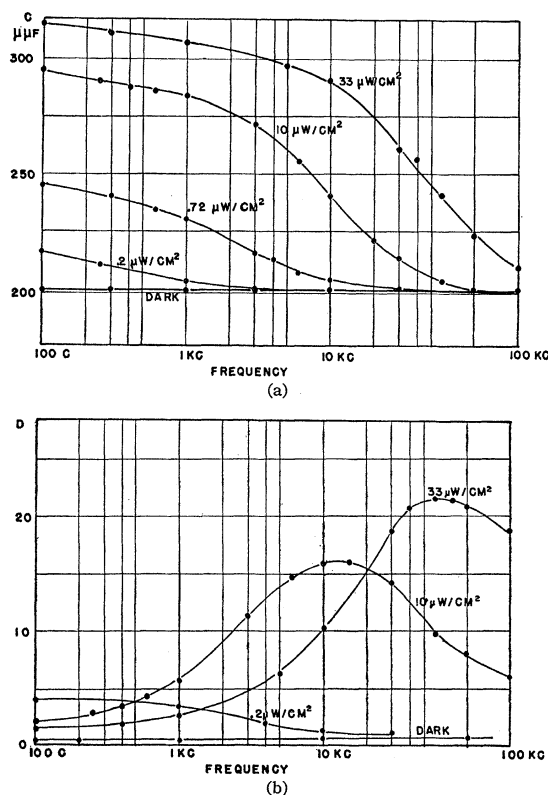

FIG. 3. (a) Capacity and (b) dissipation factor *versus* frequency at various light intensities for DuPont powder 1301. This phosphor has no dielectric change. The capacity curves come together at high frequencies. The nonuniform irradiation with respect to the surface of the sample causes the difference in peak heights of the D curves. The differences in the flat portions of the C curves at higher intensities and low frequencies may be due to the barrier effect at the negative electrode. Applied voltage: 3 v.

approximation for the model is to consider a large number of networks similar to the one shown in Fig. 2 in parallel. The values of R, C_p, and C_A in this case are distributed about mean values for each of these parameters. This requires a wider frequency range for the transition of the capacity curve between the asymptotes. Also a deviation from the theoretical model occurs in the low-frequency range at high light intensity where an increasing C rather than a flat response is measured. This region, however does not influence the results obtained in this investigation. One might suspect that for the data presented in Fig. 4(a) the flat portion of the curves are in a region where $R \ll (\omega C_p)^{-1}$ and that at sufficiently high frequencies C would fall to the dark capacity. If this were the case the drop to the dark capacity would be observed within the measured frequency range for some lower value of light intensity. However, additional measurements taken at very low light intensities show that this was not the case. The curves remained parallel to the dark curve and the height of the curves increased continuously with increasing light intensity while the dissipation factor was low and the D curves were the same within the experimental error of this measurement (Table II).

Decay-time measurements at both room temperature and liquid nitrogen temperatures have been taken for several powders. These data are shown in Fig. 5. It is seen that for those phosphors which have solely a
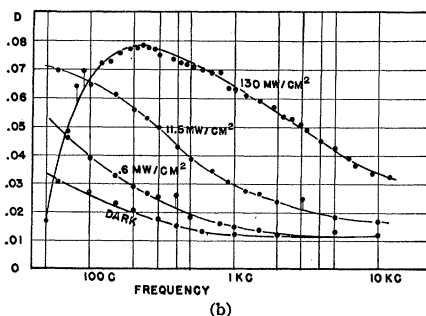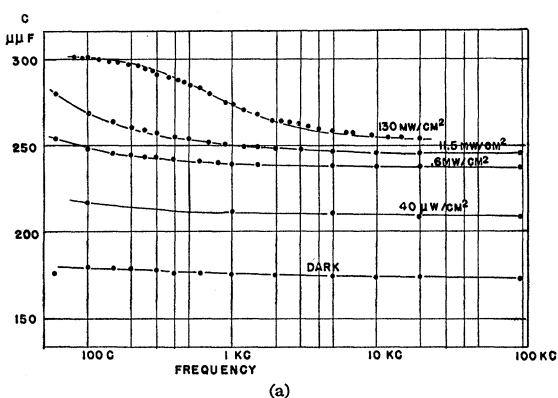

FIG. 4. (a) Capacity and (b) dissipation factor *versus* frequency for DuPont 1619 powder. Resistance change becomes important at high light intensities only. Applied voltage: 3 v.
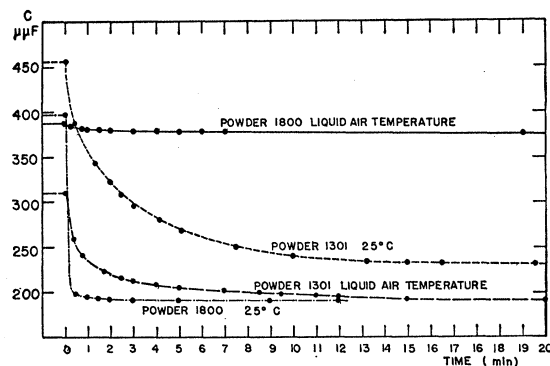

FIG. 5. Time dependence of the capacity decay after the light is turned off at $t=0$. Stimulation intensity 275 μw/cm^2.

photoconductivity the decay times are approximately the same at liquid nitrogen temperature as at room temperature. This is not found to be the case, however, in the phosphors exhibiting the photodielectric effect. Here one finds that the decay time at room temperature is considerably different from that observed at low temperature. At room temperature the decay is similar to a phosphor having only a photoconductivity. At liquid nitrogen temperature, on the other hand, one observes a slower decay finally reaching a constant value of capacity much higher than a dark value. This result is in agreement with the observations of Garlick and Gibson. The powder may be returned to its dark value by increasing the temperature without illumination. The decay of the low-temperature capacity change was found to proceed very rapidly in the vicinity of $-100°$C (0.01 ev).

For powders which exhibit a dielectric change the dc photoconductivity behaves in quite a different manner from the ac conductivity at liquid nitrogen temperature. After the illumination is removed the dc resistance returns to the dark value in a time depending on the persistance of the phosphor. The capacity change stimulated by the illumination remains constant for a

TABLE II. Data for C and D *versus* frequency at low light intensities. RCA F 2039 powder. The D curves are practically the same for all four light levels, but the C is rising gradually from the values for the dark level. The C curves are parallel to each other. Applied voltage 1.5 v.

| Frequency cycles/ sec	Dark		0.14 μw/cm^2		0.33 μw/cm^2		0.69 μw/cm^2	
	C	D	C	D	C	D	C	D
10^2	176.2	0.046	178.6	0.039	181	0.04	181.0	0.038
2×10^2	174.6	0.035	177.0	0.030	178.7	0.032	179.0	0.029
4×10^2	172.3	0.025	175.1	0.023	176.8	0.024	177.4	0.022
7×10^2	171.2	0.022	174.0	0.020	175.6	0.022	176.2	0.020
10^3	170.6	0.021	173.2	0.019	175	0.020	175.5	0.018
2×10^3	169.4	0.018	172.0	0.017	173	0.018	174.4	0.016
4×10^3	168.2	0.014	171.0	0.013	172.4	0.015	173.3	0.013
7×10^3	167.4	0.013	170.3	0.012	171.5	0.013	172.6	0.012
10^4	167.1	0.012	169.8	0.011	171.1	0.013	172.2	0.011
2×10^4	166.6	0.010	169.2	0.011	170.4	0.012	171.6	0.011
4×10^4	165.7	0.008	168.5	0.0084	169.8	0.012	171.2	0.009
7×10^4	165.5	0.007	168.2	0.0084	169.3	0.009	170.5	0.008
10^5	165.3	0.007	168.0	0.0084	169.0	0.009	170.4	0.0074
2×10^5	164.9	0.008	167.5	0.0090	168.6	0.010	170.0	0.010
3×10^5	164.6	0.008			168.5	0.010		
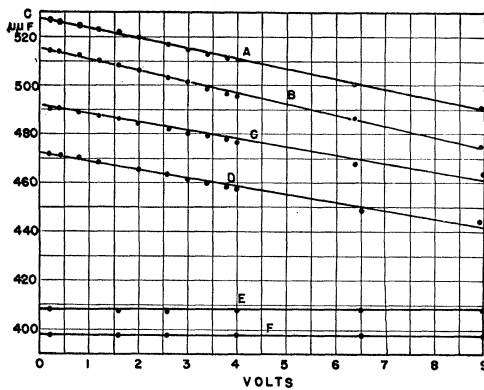
FIG. 6. Voltage dependence of capacity. The D values were not voltage dependent. Thickness of the sample 0.014 cm. Curves A and C have been measured at 62 μw/cm^2, B and D at 15 μw/cm^2, E and F in dark: A, B, E at 100 cps and C, D, F at 10 kc/sec.

long time after the dc resistance has returned to the dark value. For example, in powder 1619 a sample whose capacity dark value was 193 $\mu\mu$f increased to 399 $\mu\mu$f when irradiated (10 μw/cm^2). After removal of the light source, the capacity dropped to 382 $\mu\mu$f and remained constant. The ohmic resistance for the same light intensity was 80 megohms. Removing the light source returned the sample in a few seconds to 4×10^6 megohms which was the measured unquenched dark resistance. The quenched sample had a dark resistance of 4×10^7 megohms.

Measurements have been taken on the voltage dependence of the capacity change in the various powders; similar measurements have been reported by Roberts.[5] It is seen from the data presented in Fig. 6. for powder 1619 that the capacity decreases with increasing applied voltage. This negative slope feature is general for all the phosphors which were investigated. It has been suggested that the voltage dependence might be explained by the existence of a resistance barrier within the grains of the phosphor.[6] For a fixed light intensity as the voltage is increased the barrier width increases thereby lowering the measured capacity. One would expect for an increasing

light intensity at a fixed voltage that the density of conduction electrons increases throughout the sample such that the effective barrier width is reduced with a corresponding increase in measured capacity. The fact that this increase does not occur in powder 1301 while it does occur in 1619 appears to indicate that the concept of the barrier layer is unsatisfactory as an explanation of the capacity change. Furthermore, such a hypothesis would not conform with the observations made at the low temperature. It appears more likely that a real change in dielectric constants occurs in some phosphors when irradiated.

The dielectric effect depends on the particular phosphor, the activator, the light intensity, and the temperature of the sample. In some cases it is found that this change may be higher than 100%.

The dielectric change may be more satisfactorily explained by trapped electrons rather than electrons in the conduction band oscillating out of phase with the applied field. It appears unlikely that the persistance of the capacity change at liquid nitrogen temperature after the removal of the light source could be attributed to free electrons. The decay times are extremely long (several hours) in this case as contrasted with the fast decay (several seconds) of the dc photoconductivity. The notion of trapped electrons also presents difficulties. If the effect is to be attributed to traps one must assume an extremely large polarization of the traps. The Clausius-Mossotti formula may provide a rough estimate for the polarizability of the trapped electrons necessary to account for the observed dielectric change. If one assumes a maximum trap density of 10^{17} per cm^3 then the radius of the traps obtained is approximately 10^{-6} cm. Shallow traps are required as it was found that the samples at liquid nitrogen temperature could be returned to the dark value by a relatively slight increase in temperature. The low temperature capacity change was found to decay very rapidly (fraction of a minute) in the vicinity of $-100°C$. Further investigations are being carried out and shall be reported in the near future.

The authors are indebted to Dr. W. J. Ramm for his frequent consultations and suggestions during this investigation.

[5] S. Roberts, J. Opt. Soc. Am. 43, 590 (1953).
[6] H. Kallmann (private communication).