Some Characteristics of Zinc Oxide Phosphor

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Zinc oxide is well known as a typical oxide semiconductor and many investigations have been made concerning it. Its characteristics are quite complex compared with those of other materials. It may be said that this complexity is due to the divalency of the constituting ions and the difficulty of preparing prefect crystals. Moreover, since zinc oxide is not a purely ionic crystal, one must take into account the homopolar nature of the binding. Although important progress has been made by the recent studies on the single crystal, there remain many ambiguities. A review of the present status has been given by Heiland, Mollwo and Stöckman[1].

On the other hand, zinc oxide has been used for many practical purposes, for instance, as a catalyst and photocatalyst for a series of chemical reactions, and as a phosphor with very fast decay time. In addition, it may play an important role in future in the "Electrofax" process of photographic duplication in which the photoconductivity of zinc oxide is utilized. These applications depend in a direct way on the electronic processes in zinc oxide. As a phosphor, zinc oxide has never been a subject of such extensive investigations as have been made on other similar materials, i.e. zinc and cadmium sulfides. In this report, several characteristics of zinc oxide phosphors will be described.

1) G. Heiland, E. Mollwo and F. Stöckman, "Solid State Physics", Vol. 8, Academic Press, New York (1959), p. 193.

Experimental and Results

Sample Preparation. — The samples were prepared by firing pure zinc oxide at several temperatures from 950 to 1200°C in an atmosphere of air, forming gas, hydrogen or oxygen for various durations. In some samples, many kinds of impurities were intentionally added before firing. Only the phosphors fired in reducing atmosphere give bright green luminescence. The phosphors fired in air emit yellowish green luminescence and those fired in an oxidizing atmosphere dark orange luminescence. Except in the case of a phosphor containing lead as an activator, effects of added impurities on the luminescence spectrum do not appear clearly. Neither chlorine nor bromine functions as a coactivator. A firing in hydrogen atmosphere at 1000°C for 3 min. produced a phosphor emitting intense luminescence. Because of the strong intensity of the green luminescence, one will be concerned with it in the experiments described below.

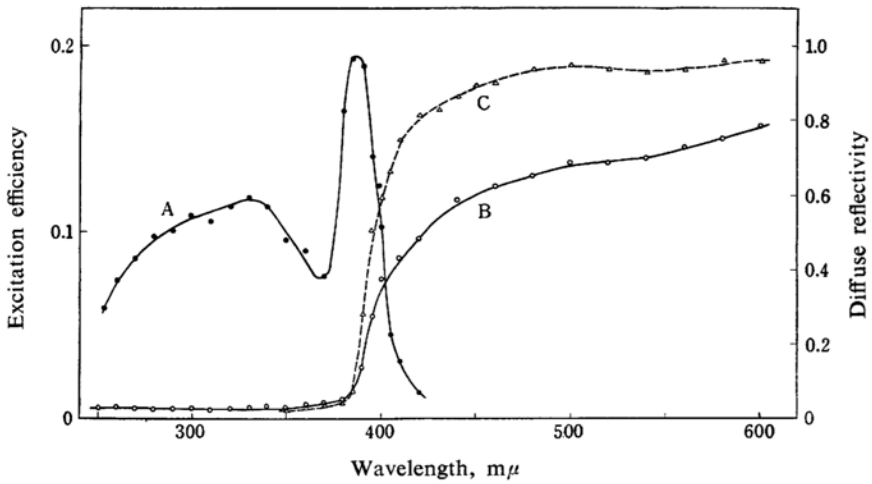

Fig. 1. Excitation and reflectivity spectra of zinc oxide.

A: Excitation efficiency of zinc oxide fired under reducing conditions.
B: Diffuse reflectivity of the same sample as A.
C: Diffuse reflectivity of zinc oxide fired under oxidizing conditions.

Luminescence Spectrum.—The luminescence spectrum was measured at both room and liquid air temperatures. The peak of the green luminescence is located at about 5050 Å and does not shift with temperature, but the spectral width decreases with decreasing temperature. This is in agreement with the published data[2].

Reflection and Excitation Spectra.—The reflection and excitation spectra were measured with the apparatus made in this laboratory[3]. As examples, some results are shown in Fig. 1. Here, the value of excitation efficiency is defined as the ratio of the number of luminescence photons to that of the incident exciting photons.

The absorption edge of zinc oxide is about 3900 Å at room temperature. The sample fired in an oxidizing atmosphere has a steep rise in reflectivity and a slight absorption at longer wavelengths. On the other hand, for the sample fired in a reducing atmosphere the rise in reflectivity is gradual and a notable absorption extends over the whole wavelength region measured. For the sample fired in stronger reducing condition, a larger absorption results.

There is a remarkable peak in excitation spectrum at the position of the absorption edge. The peak value of the excitation efficiency depends on the sample and amounted to 0.31 in the most efficient phosphor. It has no apparent correlation with the increment in absorption. The excitation decreases with decreasing wavelength of excitation and there are some structures. A similar behavior of excitation spectrum has been reported for zinc sulfide[4] and cadmium sulfide[5].

Temperature Dependence of Luminescence Intensity.—The temperature dependence of luminescence intensity was measured under excitation with both 2537 and 3650 Å radiation. As shown in Fig. 2, the characteristics are similar for the

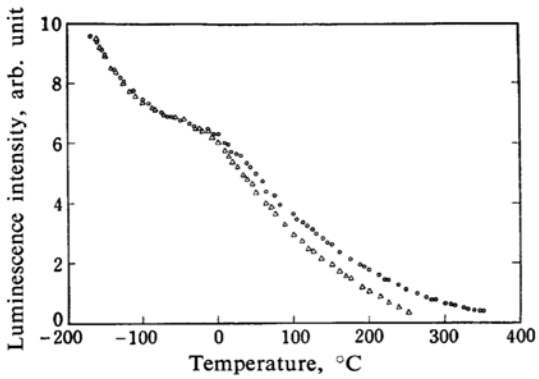

Fig. 2. Temperature dependence of luminescence intensity under 3650 Å excitation (○) and under 2537 Å excitation (△).

two sorts of exciting radiation. The intensity decreases with increasing temperature and the curves have an interesting shape in the neighborhood of 0°C. The author's results are different from those reported by Gobrecht et al.[6]

Decay of Luminescences.—The decay of luminescence was measured with an oscilloscope

2) F. J. Studer and L. Gaus, "Soild Luminescent Materials", John Wiley & Sons, Inc., New York (1948), p. 258.
3) Y. Uehara, I. Masuda and Y. Kobuke, to be published.
4) R. H. Bube, *Phys. Rev.*, **90**, 70 (1953).
5) C. C. Klick, ibid., **89**, 274 (1953).
6) H. Gobrecht, D. Hahn and K. Scheffler, *Z. Physik*, **139**, 365 (1954).

Tektronix Model 513D under pulse excitation of cathode ray and care was taken not to distort the fast signal. The luminescence decays very fast and exponentially with time constant of 0.4 μ sec., which is about an order of magnitude smaller than that reported by Gobrecht et at.[6]

After interruption of photoexcitation it was found a phosphorescence of very weak intensity but with long persistence. This phosphorescence is excited more strongly by 2537 than by 3650 Å radiation. The decay is neither simple monomolecular nor bimolecular type but is represented approximately by t^{-n} for a period of time between 1 and 20 min. following the interruption of excitation. Here n has the value 0.9 ± 0.1 depending on the sample and the condition of excitation. The phosphorescence intensity at one minute after interruption of excitation is smaller by more than three orders of magnitude than the steady state intensity under excitation.

Atmosphere Dependence of Luminescence Intensity.—It was found that the luminescence intensity under photoexcitation becomes stronger when the ambient atmosphere of the phosphor is evacuated with a rotary vacuum pump. Fig. 3 illustrates the change of luminescence intensity with time for the processes, excitation on, pumping start, admission of air and excitation off. Average values on several measurements are shown in Table I for the following quantities; the ratio of the luminescence intensity increase ΔI due to evacuation to the steady state luminescence intensity I, in air and the rise time T_r and the decay time T_d of the processes. It was ascertained that $\Delta I/I$ is larger for the weak excitation than for the strong excitation; that is, the proportionality between excitation and luminescence intensities is not satisfied. Here, the intensity ratio of strong to weak excitation is roughly 10. T_r is probably determined by the speed of the evacuating system, and T_d is in dependent on the exciting condition. It could not be detected the slow variation of luminescence intensity compared with T_r and T_d within the experimental accuracy. The light

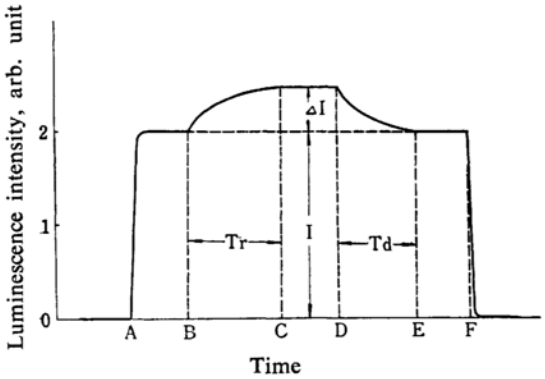

Fig. 3. Variation of luminescence intensity with ambient atmosphere.

A: Excitation on, B: pumping start, C: steady state luminescence intensity in vacuo, D: admission of air, E: steady state luminescence intensity in air and F: excitation off.

TABLE I

Excitation	$\Delta I/I$	T_r	T_d
Strong 2537 Å	0.14	1.7 min.	50 sec.
Weak 2537	0.18	1.8	54
Strong 3650	0.10	1.6	62
Weak 3650	0.17	1.3	44

intensity reflected from magnesia smoke placed at the same position as the phosphor is independent of the condition of evacuation. Therefore, the variation of luminescence intensity described above can not be attributed to any other causes than the phosphor itself.

Then the author investigated the relationship between the luminescence intensity and the ambient pressure under various kinds of simple atomospheres, such as hydrogen, oxygen, dry air, and mixed vapor of water and ethanol. Of these atmospheres, hydrogen, oxygen or dry air, when passed through a liquid air trap, exhibits no recognizable effect on luminescence intensity. On the other hand, water or ethanol vapor decreases the luminescence intensity

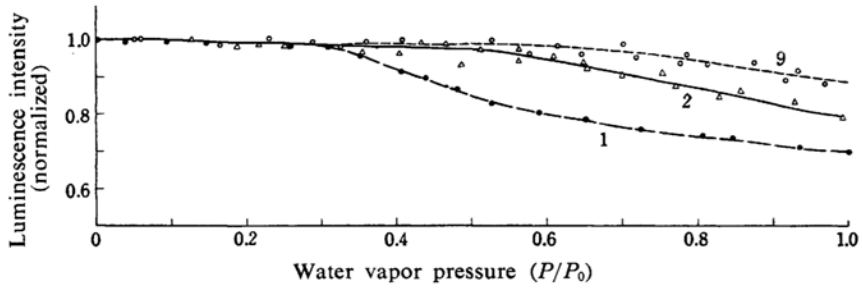

Fig. 4. Dependence of luminescence intensity on water vapor pressure for various exciting intensities (at 30°C). Relative exciting intensity is indicated in the figure and P_0 is the saturated vapor pressure.

considerably. Although the results are not always reproduced quantitatively, some of them are shown in Fig. 4 for three excitation intensities. From this figure it is seen that the luminescence intensity suffers quenching for the pressure P which is not so small compared with the saturated vapor pressure P_0. In the process of these measurements, photoadsorption or photodesorption of the vapor which gives an effect to luminescence intensity did not occur to a measurable extent.

Surface Potential.—It was expected that a change in the surface potential of the phosphor might be accompanied with the variation of the luminescence intensity under the ambient atmosphere. The author measured it by the well known Kelvin method using gold as a reference electrode. When dry or wet air is admitted, the surface potential of zinc oxide becomes more positive compared with that in vacuo.

X-ray Diffraction.—From the precise measurements of the lattice constants, it is concluded that the lattice constants are independent of the conditions of preparation within an experimental error. The numerical values are in complete agreement with those reported by Bunn[7].

Discussion

The green luminescence of zinc oxide is characteristic of phosphors fired under reducing conditions, and it has been reported[8] that a stoichiometric excess of zinc is detected by a chemical analysis from a sample prepared in this way. Although there would be many kinds of lattice defects in the green-emitting zinc oxide, interstitial zinc atoms and oxygen vacancies are considered to be the dominant defects. It is customarily said that the interstitial zinc atom is the luminescence center for the green luminescence. However, according to Mollwo[9], the green luminescence is quenched when the crystal is heated in zinc vapor below 1000°C and zinc atoms diffuse in it. On the contrary, Riehl and Ortman[10] have attributed the green luminescence center to the oxygen vacancy. The energies necessary for formation and migration of the oxygen vacancy would be greater than those of the interstitial zinc atom, since the binding between oxygen and zinc should be broken for the former processes. This consideration agrees with the various conditions for the preparation of the green-emitting phosphor. For example, the efficient phosphor should be fired at higher temperatures than those necessary for the introduction of interstitial zinc atoms.

The oxygen vacancy would be able to accomodate two electrons since it has two effective positive charges in the ionic model of zinc oxide. The same conclusion can be drawn from the covalent model. The first electron would be bound tightly in the vacancy but the second loosely. To be effective as the luminescence center, it would be necessary for the vacancy to have a specific charge. The quenching of green luminescence when the electric conductivity becomes great, for example, by the introduction of excess of zinc as cited above, might be explained by this model.

The ultraviolet emission, which is known to appear in zinc oxide fired under oxidizing conditions, is not observed for these samples. Although Kröger and Meyer[11] attributed this emission to exciton recombination, still more investigations are necessary to arrive at a definite conclusion.

The author has tried an analysis of the one-dimentional configurational coordinate curves[12] based on the experimental result that the peak position of the luminescence spectrum is independent of temperature. From this analysis one may expect an absorption band by the luminescence center in the long wavelength side of the absorption edge. Although an absorption in the expected wavelength region increases as a result of the firing under reducing conditions, one can not observe the excitation of luminescence by this absorption. In additon, the intensity of this absorption does not have any apparent connection with the luminescence efficiency of the phosphor. Therefore, it is considered that this absorption is probably caused by a change of the crystal lattice due to the presence of interstitial zinc atoms.

The decay of luminescence is exponential and the time constant is smaller by one order of magnitude than the reported value. It is considered[1] that the luminescence is emitted by the recombination of electrons at the luminescence center. If it is assumed that the density of the free electron is greater than that of the emptied luminescence center during excitation, the exponential decay and the dependence of time constant upon the sample can be understood.

It might be expected that the temperature dependence of luminescence intensity is different for the two sorts of excitation, i.e. 2537 and 3650 Å radiation, because the author found the structure in the excitation spectrum and the position of the absorption edge shifts toward longer wavelengths with increasing temperature at the

7) C. W. Bunn, *Proc. Phys. Soc.*, **47**, 835 (1935).
8) E. Mollwo and F. Stöckman, *Ann. Physik*, (6), **3**, 223 (1948).
9) E. Mollwo, *Z. Physik*, **138**, 478 (1954).
10) N. Riehl and H. Ortman, *Z. Elektrochem.*, **60**, 149 (1956).
11) F. A. Kröger and H. J. G. Meyer, *Physica*, **20**, 1149 (1954).
12) K. Maeda, *J. Phys. Soc. Japan*, **14**, 478 (1959).

rate of about 10^{-3} eV./deg[13]. However, the result is not in accord with the expectation. This suggests that the excitation spectrum changes its shape with temperature. From the temperature dependence shown in Fig. 2, one expects not a single but two kinds of activation energy for the nonradiative de-excitation. In the usual way, one obtains the activation energies of the order of 0.01 and 0.2 eV. by fitting the calculated curve with the observed. However, it is not clear to what process these activation energies correspond.

The slow phosphorescence decay indicates the existence of various metastable states. Considering the *n*-type conductivity of the phosphor, these states are probably deep hole traps.

The effect of atmosphere on the luminescence intensity has been reported only for a case of oxygen on cadmium sulfide[14]. In this case, the photoconductivity of cadmium sulfide is also reduced by the oxygen ambient. It is known that the photoconductivity of zinc oxide is decreased to a large extent by the adsorption of oxygen[16]. However, one found a quenching of luminescence intensity due to molecules having the hydroxyl group but not due to oxygen. Therefore, the above phenomenon seems to have a mechanism of quenching different from that found in cadmium sulfide. As stated in the preceding section, the surface potential of zinc oxide becomes positive when either dry or wet air is admitted relative to that in vacuo. Therefore, the change in the surface potential is not a cause of the luminescence quenching. The adsorbed molecule probably has an effect to accelerate nonradiative recombination of electrons and holes at the surface. Since the absorption constant in the fundamental absorption region is of the order of 10^5 cm^{-1} [16], electron-hole pairs are created by light absorption to a depth greater than that of a range influenced by surface conditions. Therefore, the amount of quenching is relatively small.

13) E. Mollwo, *Z. angew. Phys.*, **6**, 257 (1954).
14) S. H. Liebson and E. J. West, *J. Chem. Phys.*, **23**, 977 (1955); S. H. Liebson, ibid., **23**, 1732 (1955).
15) D. A. Melnick, *J. Chem. Phys.*, **26**, 1136 (1957).
16) E. Mollwo, *Ann. Physik*, (6) **3**, 230 (1948).

Summary

Zinc oxide phosphors were prepared under various conditions. From measurements on the characteristics of the green luminescence of the phosphors fired in reducing atmosphere, the following features were observed. (1) In the excitation spectrum, there is a sharp peak at the position of the absorption edge and a gradual decrease toward shorter wavelengths with some structures. The observed maximum value of excitation efficiency is 0.31. (2) The luminescence intensity decreases with increasing temperature. The plot of intensity against temperature has an unusual shape in the neighborhood of 0°C. (3) The decay of luminescence is exponential and the time constant, 0.4 μ sec., is smaller than that previously reported by an order of magnitude. Long persistent phosphorescence is observed indicating the presence of deep hole traps. (4) The luminescence intensity decreases in a gaseous ambient of molecules having the hydroxyl group.

Standing on the present experimental results, discussions have been undertaken on the luminescence center as well as on the theoretical explanation of the observed characteristics.

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