Dependence of Luminescence on Physical Structure in Zinc Borate Compounds

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Luminescent zinc borate compounds have been prepared which can be obtained in either vitreous or crystalline form and which can be converted from one form to the other by purely physical processes. The dependence of luminescence of compounds of this type on physical structure has been investigated. It is found that changing a given compound from vitreous to granular state increases its luminescence many times. It is also found that zinc borate compounds can be made luminescent without the addition of an activator. The addition of an activator is found to result in a condensation of the emission bands and an increase in their wave-lengths. The bearing of these on the "solid solution" idea is discussed.

INTRODUCTION

L UMINESCENCE excited in certain chemical compounds by light or other types of radiation is generally considered to be a characteristic of "solid solutions." It has been asserted by various investigators that pure substances do not luminesce. A small quantity of one element, known as the solute or the activator, intimately mixed with a large quantity of another compound, known as the solvent, is supposed to give rise to a number of active centers (Lenard centers) which have the property of absorbing and reemitting energy in the form of luminescence.

There is a wide divergence of opinion as to the nature of these hypothetical centers, and the function of the activator atom in producing luminescence. It is claimed by some that in the luminescence of solid solutions the solute plays the active role while the function of the solvent is to insure the dissemination of the molecules of the activator.[1] In agreement with this view several investigators have claimed that the impurities responsible for luminescence of certain minerals can be identified by determining the wave-lengths of the bands emitted by them,[2, 3] although this has been questioned by others.[4, 5]

The emitting centers have been usually considered as consisting of molecular aggregations of the solvent linked in some way with a single activator atom (Lenard theory).

In recent years the dependence of luminescence on crystal structure has been emphasized.[6, 7] It is supposed that the emitting centers consist of crystal units of the solvent into which an activator atom has entered, either isomorphically or by absorption, thereby causing a distortion of the lattice. Working on this hypothesis, Ewles[8] computed the number of the molecules of the solvent in a crystal unit linked to one molecule of the solute, for certain luminescent compounds, by determining the optimum concentration of the solute for producing luminescence in these compounds. Cohen,[9] however, finds that Ewles' conclusions do not agree with his determinations of the optimum concentration for thermoluminescence of zinc borate glass and rejects the theory of crystal structure.

It was considered desirable, therefore, to investigate further the dependence of luminescence on the physical structure of the compounds and also to determine whether or not the presence of an activator was absolutely necessary. Certain mixtures of zinc oxide and boric acid were found very suitable for this purpose since they can be obtained in either vitreous or crystalline form, and can be converted from one form to the other, by purely physical processes, without altering their chemical compositions. The effects of such modifications on the luminescence of these compounds are given below.

[1] L. Bruninghause, J. de phys. et rad. 2, 398 (1931).
[2] Tanaka, J. Opt. Soc. Am. 8, 411 (1924).
[3] H. Haberlandt, B. Karlik and K. Przibram, Akad. Wiss. Wien. Ber. 143, 151 (1934).
[4] S. Iimori, Inst. Phys. and Chem. Research Tokyo, Sci. Papers 419, 274 (1933).
[5] F. Schmidt, Ann. d. Physik 12, 211 (1932).
[6] M. Servigne, Comptes rendus 200, 2015 (1935).
[7] E. Iwase, Inst. Phys. Chem. Research Tokyo, Sci. Papers 567, 1 (1935).
[8] J. Ewles, Proc. Roy. Soc. 129, 509 (1930).
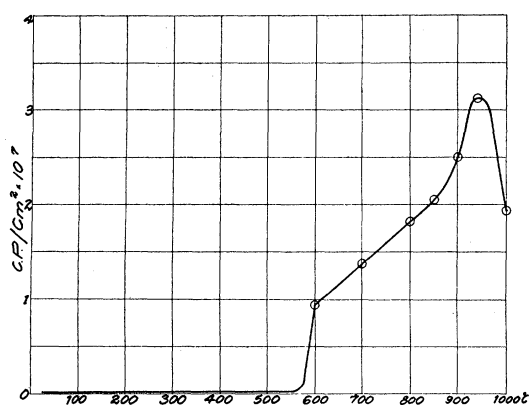[9] B. E. Cohen, J. Am. Chem. Soc. 55, 953 (1933).

FIG. 1. Variation of brightness with heat treatment temperature for fused C.P. zinc borate disk. Ordinates brightness in candlepower per cm², abscissae maximum temperatures to which the compound has been heated, transition at 600°C.

MATERIALS AND MODE OF PROCEDURE

Preparation of zinc borate glass

Zinc oxide and boric acid mixed in proportion corresponding to the formula ZnB_2O_4 and heated to a temperature of about 500°C, combine to form an amorphous mass. If this mass is heated to about 1000°C, it will fuse into a clear glass known as zinc borate glass. Zinc borate glasses with a much higher zinc oxide content than that corresponding to the above formula can be prepared. Such glasses can be made to luminesce by the addition of activators.[10] If the zinc oxide content of the mixture be gradually increased, a point is reached when the fused mass may become, on cooling, either vitreous or crystalline, depending upon the rate of cooling. This critical mixture, corresponding approximately to 57 percent zinc oxide and 43 percent boric acid, was used in the experiments described below and is referred to as zinc borate compound for want of a more definite term.

A mixture of zinc oxide and boric acid in the above proportion is fused in a platinum crucible in an electric furnace. A drop of the fused material is then quickly squeezed between two brass plates to a small disk of clear glass, 0.5 mm thick and 10–15 mm in diameter. This quick cooling is necessary to obtain a clear glass. If the fused material is allowed to cool slowly, a crystalline mass will result. These disks are

[10] Nyswander and Cohn, J. Opt. Soc. Am. **20**, 131 (1930).

quite stable at ordinary room temperatures. They have the characteristics of the vitreous state, and will begin to soften at about 650°C with no definite melting point.

Conversion into crystalline state

One of these clear disks is placed on a platinum plate and introduced into an electric furnace, at a temperature of 600°C. In a few minutes the disk loses its transparency. It becomes opaque and granular in appearance. After the transformation is completed the disks can be raised to much higher temperatures without losing their shape. They have the characteristics of a crystalline mass with a fairly definite melting point at about 1000°C. They can be fused again at higher temperatures and converted back into vitreous state as described above.

Measurements of luminescence

A large number of such disks were prepared both from C.P. materials and also from materials to which an activator had been added, and the luminescence produced in these, both in vitreous and crystalline states, was examined.

Excitation was produced by means of an iron spark, a quartz mercury arc, cathode rays and rays from radioactive materials. For quantitative measurements of brightness excitation was produced only with radium disks to insure the absorption of equal amounts of energy by the transparent and nontransparent forms of the
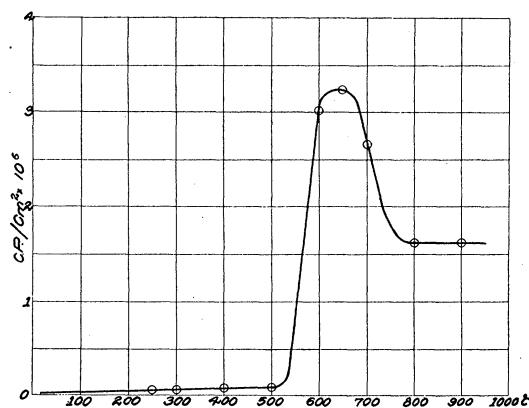

FIG. 2. Variation of brightness with heat treatment temperature in fused zinc borate disk activated with manganese. Ordinates brightness in candlepower per cm², abscissae maximum temperatures to which the material has been exposed. Transition takes place between 500° and 600°C.

material. The radium disks and the special type of photometer used in these measurements have been described in a previous paper.[11] A quartz spectrograph was used to determine the wavelength distribution of the emission bands. All measurements were made at the room temperature.

<div align="center">RESULTS</div>

Luminescence of pure zinc borate compounds

A clear zinc borate glass disk prepared from C.P. materials in the above proportion does not show any appreciable luminescence with such exciting sources as mercury arc, iron spark, or rays from radioactive elements. An appreciable luminescence appears in it on converting it into the opaque form at 600°C.

The opaque disk can now be exposed to various higher temperatures and its luminescence measured after cooling. Fig. 1 gives the variation in the luminescence of such disks with the maximum temperatures to which they have been exposed. It is seen that the maximum brightness is obtained at about 950°C, after which the luminescence begins to decline as the material approaches its melting point. At higher temperatures it can be fused and converted into vitreous form with complete loss of luminescence. The luminescence can, however, be recovered by going through the same process of reconverting it into crystalline form. This conversion from crystalline to vitreous form and *vice versa*, with appearance and disappearance of luminescence, can be repeated indefinitely, showing that the cycle has not produced any permanent changes in the material.

Luminescence of activated zinc borate compounds

Addition of 1 percent manganese, produces some distinct changes in the luminescence of this compound. The fluorescence is increased, the phosphorescence is diminished, the wavelength of maximum emission becomes much larger and the emission bands become much narrower, but the dependence of luminescence on the physical structure of the material is the

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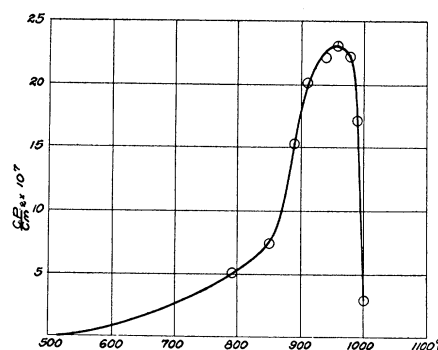[11] D. H. Kabakjian, Phys. Rev. **44**, 618 (1933).

FIG. 3. Variation of brightness with heat treatment temperature in activated zinc borate powder. Ordinates brightness in candlepower per cm², abscissae maximum temperatures to which the compound has been raised.

same as in the pure compound. The activated compound, fused into a clear glass disk, shows very faint luminescence. This is increased tremendously when the disks are divitrified at 600°C. Fig. 2 shows the rise in brightness of such a disk with the maximum temperatures to which it has been exposed. It is seen that the temperature of maximum brightness in this case is 650°C.

Both pure and activated compounds can also be made luminescent by heating the amorphous mixtures to temperatures below the fusion point. The materials obtained in this way, however, do not luminesce as intensively as those obtained by divitrifying the fused compounds. Fig. 3 gives the rise in brightness of such a mixture, with the temperature of heat treatment, for a compound activated with manganese.

Nature of the emission bands

The emission of pure zinc borate consists of a single diffuse band in the violet, extending far into the ultraviolet region, with a maximum emission at about 4000A. The activated compound can be made to give a band in the red or in the green region. These are comparatively narrow bands. Ordinarily both bands are present and overlap, giving the appearance of a continuous band but by careful control of temperature they can be distinguished as two distinct bands. In Fig. 4, "a" is a spectrogram of the emission from the pure compound and "b" from the activated compound giving the red band, when bombarded by cathode rays in a cold cathode-ray discharge tube operated at about
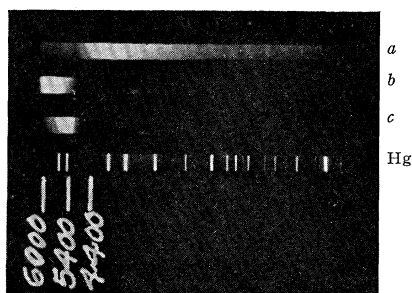
Fig. 4. Cathode-ray spectrogram of the pure and activated zinc borate compounds, "*a*" pure zinc borate, "*b*" and "*c*" manganese activated zinc borate heated to different temperatures.

8000 volts.[12] Both compounds were heated to 950°C. "*c*" is also from an activated compound heated to a much lower temperature. The green band predominates in this case.

Discussion

Several conclusions can be drawn from these experiments. It is seen that luminescence is closely connected with the physical structure of these compounds. A change from vitreous to granular state increases the brightness of the activated zinc borate more than 30 times. The ratio is even greater in the case of pure zinc borate. Whether the structure is microcrystalline or not cannot be definitely stated at this time but this seems quite probable. Assuming a crystalline structure, it appears that the nature of the emissions, and hence the nature of the emitting crystals, is controlled by the temperature of heat treatment as well as by the presence of the activators. It is also seen that pure zinc borate can be made luminescent without the addition of an activator. Although absolute purity is not claimed for this compound, the intense luminescence of the C.P. mixtures can hardly be explained as due to some undetected impurity, since the nature of luminescence given by the activated compound is quite different from that of the pure compound, as seen above.

The luminescence of pure compounds has been claimed in previous communications from this laboratory.[13, 14] In recent years similar claims have been made by others.[15] If it be assumed that luminescence results from displacement of electrons to higher energy levels which may exist in an orderly arrangement of molecules, there is no reason to assume that pure substances cannot luminesce. Whether or not luminescence can be excited in a given solid will depend upon the existence or not existence of unoccupied energy levels to which electrons can be displaced, and not necessarily upon the presence of an impurity. On the other hand, the function of the impurity seems to be to lower these energy levels, as indicated by the abrupt change in the wave-length of the emission bands when an activator is used. If this law holds generally for other crystals, we might expect many pure crystals to show luminescence in the ultraviolet region. Addition of activators to these would simply bring the luminescence within the visible range, thereby creating the impression that the luminescence is produced by the activator. This seems to be true for a number of crystals under investigation, the results of which will be published in the near future. It is also possible that activator atoms create unoccupied energy levels in some crystals where none existed before. In any case the generally accepted idea of luminescence as due to active centers requiring an impurity as a nucleus seems subject to modification.

[12] This voltage was found sufficient to excite all the wave-lengths as no additional wave-lengths appeared on such spectrograms when the specimens were excited by α-rays of polonium at high speed β-rays from radium B+C.

[13] J. A. Rodman, Phys. Rev. 23, 478 (1924).
[14] L. E. Smith, Phys. Rev. 28, 432 (1926).
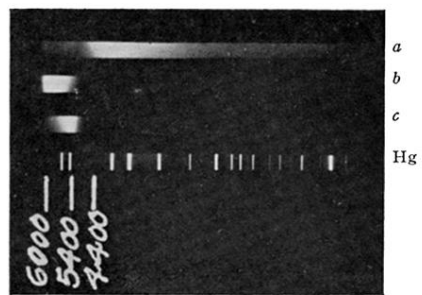[15] O. Glasser and I. E. Beasler, Phys. Rev. 47, 470 (1935).

FIG. 4. Cathode-ray spectrogram of the pure and activated zinc borate compounds, "*a*" pure zinc borate, "*b*" and "*c*" manganese activated zinc borate heated to different temperatures.