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Luminescence of Pure Radium and Barium Compounds

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Luminescence, excited in some carefully purified crystalline barium and radium compounds by alpha-, beta-, and gamma-rays has been examined. It is found that these compounds show a faint luminescence at ordinary room temperatures. When the compounds are heated to various temperatures and then cooled, they show a continuous increase in luminescence with increase of temperature of heat treatment until a maximum is reached. Heat treating at higher temperatures diminishes the brightness. The temperature of maximum brightness is not directly related to the melting point of the individual compounds. The maximum brightness in some cases was several hundred times the initial brightness of unheated crystals. No abrupt changes in intensity of luminescence, such as might be due to changes in crystalline form, were detected. The bearing of these experiments on the modern theories of luminescence in crystalline solids is discussed.

In a previous paper,[1] the writer described some experiments to prove that certain zinc borate compounds can be made luminescent in a state of purity. The compounds were obtained in a vitreous form by fusion in an electric furnace at about 1100°C. The clear zinc borate glass so obtained does not show any appreciable luminescence. If, however, it is devitrified by heating for a few minutes at 600°C, a strong luminescence of a purple color is developed. The structural change from the vitreous to crystalline state was verified by Debye-Scherrer photographs of the samples, which were kindly obtained for me by Professor B. E. Warren of the Massachusetts Institute of Technology.

The close relationship between crystalline structure and luminescence in inorganic solids, indicated by the above experiment, is already well established. A general theory of luminescence based on the existence of electronic energy states in a crystal lattice, has been found quite successful in explaining a large number of experimental observations.[2] Most of the investigations are carried on, however, on activated crystals, i.e., on crystals containing an impurity atom.

The possibility of luminescence in very pure crystals was doubted by most investigators until very recent times. Since the luminescence of some pure crystals is now generally admitted,[3] the nature of the luminescent centers has become a problem of theoretical interest. The writer has found that, with rays from a radioactive source, luminescence can be excited in a number of pure crystals. The initial brightness in most of these is rather faint, but in some cases it can be increased several hundred times by a proper heat treatment.

Most impurity-activated phosphors also require heat treatment in their preparation, but in these cases the object is either to insure a diffusion of the impurity into the crystal lattice of the base material (solid solution) or to develop a crystalline structure in the mixtures when these are obtained in the form of fine precipitates. In the experiments described below, these considerations do not exist, since the compounds are obtained initially in crystalline form and no impurity is added. Raising the pure compound to a given temperature and then cooling produces a modification in its crystalline state which makes luminescence possible. It was considered desirable, therefore, to investigate the relation between the temperature of heat treatment and intensity of luminescence.

MATERIALS AND MODE OF PROCEDURE

The luminescence of the following compounds has been investigated: $RaBr_2$, $RaCl_2$, $RaSO_4$, $BaBr_2$, $BaCl_2$, $BaSO_4$. Pure $RaBr_2$ was obtained from a mixture of radium bromide and barium bromide by a large number of successive crystallizations with distilled water and pure HBr. Its weight and radium-element content corresponded to pure anhydrous $RaBr_2$. Radium sulphate was

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[1] D. H. Kabakjian, Phys. Rev. **51**, 365 (1937).

[2] F. Seitz, Trans. Faraday Soc. **35**, 74 (1939).

[3] N. Riehl, Ann. d. Physik (5) **29**, 637 (1937); S. Rothschild, Zeits. f. Physik **108**, 24 (1937); W. H. Byler, J. Am. Chem. Soc. **60**, 1247 (1938).

obtained from pure radium bromide by precipitation with C.P. sulphuric acid. The precipitate then was dissolved in hot concentrated sulphuric acid and was recrystallized by evaporation. The crystals were well formed and fairly large. Barium compounds were similarly purified by repeated recrystallizations.

The pure compounds were placed in hard glass or silica tubes of 1.5–2.5 mm outside diameter and 0.2 mm wall thickness. They were heated to various temperatures in an electric furnace until equilibrium was established and their brightness was measured after cooling to room temperature. On account of their small size, the samples reach room temperature in a few minutes. Tests showed that the luminescence was not affected by the rate of cooling. In radium compounds the excitation is produced chiefly by alpha-rays. In the case of barium compounds, a small quantity of radium bromide or radium sulphate was added to the corresponding barium salts for an alpha-ray excitation. Since there is a possibility that the added radium might act as an impurity activator, these were investigated by a different process which eliminates this uncertainty. The barium salt was placed between the walls of two coaxial glass or silica tubes closed at the bottom. The thickness of the barium salt was about 0.6 mm. A thin-walled monel metal tube containing 6 mg of radium element in sulphate form was fitted into the inner tube, having a wall thickness of 0.1 mm. The radium tube could be removed during the process of heating the salt. The excitation in this case is produced by beta- and gamma-rays of constant intensity since the radium is in equilibrium with its decay products.

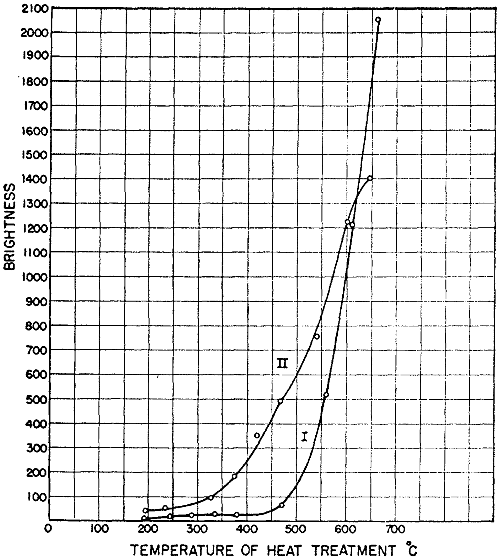

FIG. 1. Growth of brightness, in arbitrary units, of pure radium compounds with the temperature of heat treatment. Curve I, anhydrous radium bromide. Curve II, radium sulphate.

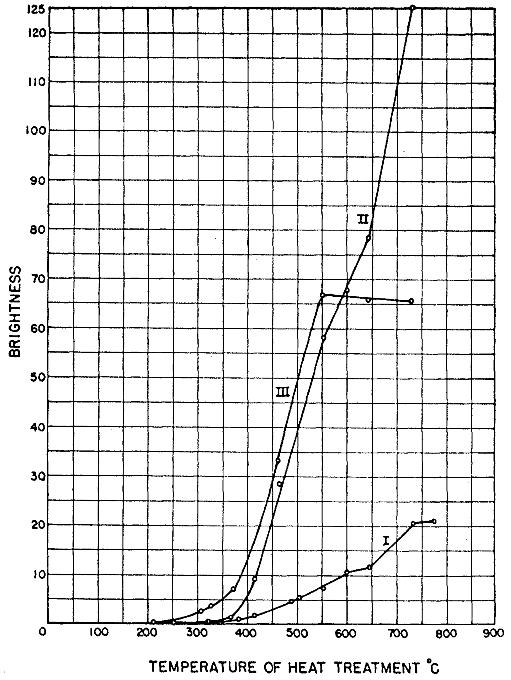

FIG. 2. Growth of brightness of pure barium bromide with the temperature of heat treatment. (I) Barium bromide mixed with 0.24 percent radium bromide, (alpha-ray excitation). (II) barium bromide mixed with 1.2 percent radium bromide. (III) barium bromide excited with beta- and gamma-rays from a sealed radium tube.

The results obtained by this method, which were in general similar to those obtained from mixtures of radium and barium compounds, showed that the production of luminescent centers is independent of the presence of radium atoms.

The brightness measurements were made on a modified Lummer-Brodhun photometer, which has been described in a previous paper.[4]

RESULTS

A large number of determinations made on the temperature-brightness relationship of these

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

compounds gave similar results. Some typical curves are indicated below. Fig. 1 gives the variation of brightness for pure radium bromide and radium sulphate with the temperature of heat treatment from 200° to 650°C. It is seen that the brightness rises as a continuous function of this temperature, reaching a maximum at about 650°C for both compounds. This maximum activation temperature apparently is not related to the melting points of the two compounds. The ratio of maximum brightness to the initial brightness for radium bromide is 182 and for radium sulphate 35.4. This ratio refers to visible luminescence only. Since a large portion of the radium sulphate emission lies in the ultraviolet region, the emission energy of the two compounds might approach equality. No attempt was made to determine this point.

Figure 2 gives the activation-temperature relationship for barium bromide. Curves I and II refer to compounds containing 0.24 percent and 1.2 percent of radium bromide, respectively. Excitation in these was produced chiefly by alpha-rays.

Curve III was obtained by beta- and gamma-ray excitation from a sealed radium tube. The curves show the same activation-temperature relationship, although there are some differences in the two types of excitation. The ratio of maximum brightness in samples I and II is roughly proportional to their radium content and therefore to the intensity of excitation. In Fig. 3 the temperature effect is shown for barium chloride also excited by beta- and gamma-rays.

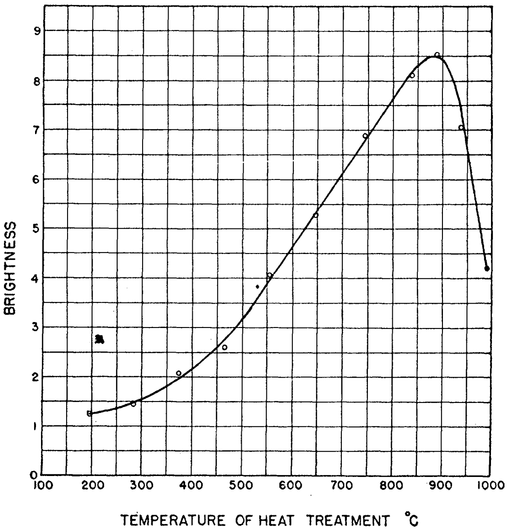

Fig. 3. Growth of brightness of pure barium chloride with the temperature of heat treatment. Beta- and gamma-ray excitation.

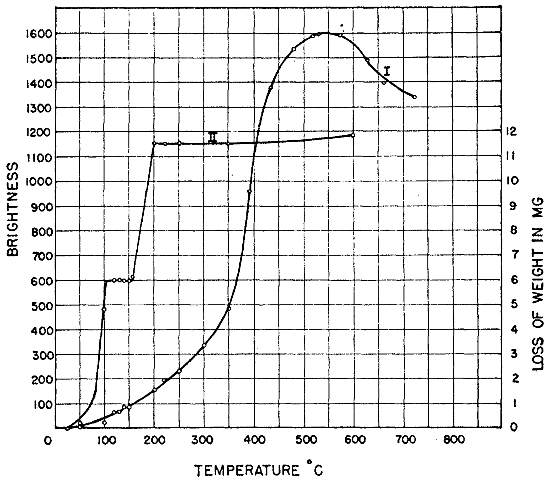

Fig. 4. Curve I. Growth of brightness of pure $BaBr_2 \cdot 2H_2O$ with the temperature of heat treatment (beta- and gamma-ray excitation). Curve II. Loss of water of crystallization during heating. Ordinates to the right.

Crystallization at Lower Temperatures

The crystals in the above experiment were produced by boiling the respective solutions to saturation. The bromides contain two molecules of water of crystallization. Complete dehydration of this compound required, under the conditions of these experiments, prolonged heating at 200°C. The boiling point of the sulphate solution in concentrated sulphuric acid is about 190°C, therefore the initial brightness readings had to be started with a heat treatment temperature of 200°C. In the case of bromides, it is possible to extend this part of the curve to a much lower temperature. A saturated solution of barium bromide was prepared at room temperature and placed in a desiccator. A few large clear crystals were produced in the solution by slow evaporation extending over several days. It is assumed that these crystals approximated a perfect lattice better than those produced from hot solutions. The crystals were dried in a desiccator in the same way without heating. This compound, having a formula $BaBr_2 \cdot 2H_2O$ was ground, and its activation-temperature relationship was ex-

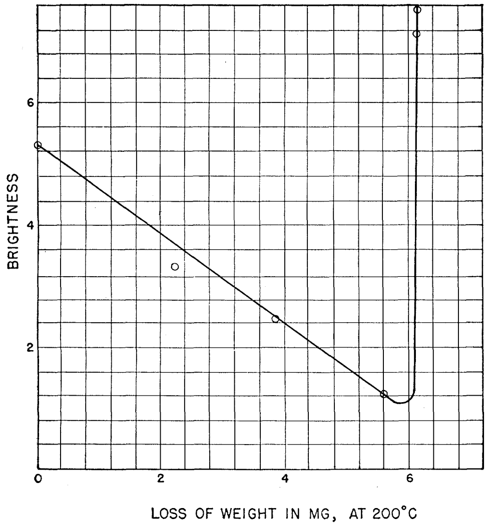

FIG. 5. Variation of brightness with gradual removal of water of crystallization at 200°C.

amined in the same way by beta- and gamma-ray excitation. The loss in weight due to dehydration was determined at the same time.

In Fig. 4, Curve I gives the rise of brightness with the heat treatment temperature. Curve II shows loss of weight due to dehydration. The initial brightness in this case was very low and difficult to measure. The ratio of maximum brightness to the initial brightness was approximately 300.

EFFECT OF WATER OF CRYSTALLIZATION

The removal of the second molecule of water of crystallization had a very marked effect on the intensity of luminescence. As the temperature was raised from 150° to 200°C, the luminescence began to decrease and continued to do so until all of the moisture was removed, when it suddenly rose again. This relation is shown in Fig. 5. A similar effect might have been produced during the removal of the first molecule of water but was not detected because of the faintness of luminescence at the lower temperature. The points on the smooth curve in Fig. 4 represent equilibrium values of brightness.

THE NATURE OF EMISSION BANDS

The compounds were sealed in clear silica tubes and their luminescence was examined by means of a quartz spectrograph. The emission of the sulphates consists of a diffuse band extending from 5800–3000A with a maximum at about 4050A. The bromides give a somewhat overlapping double band with maxima at 4700 and 3000A. The luminescence bands of the same compounds, after a small percentage of Mn or Sa was added to them were also obtained under similar conditions. The added activator in these cases produced its own band, quite distinct both in structure and wave-length, somewhat at the expense of the luminescence of the pure compound, but did not completely supersede it as in the case of zinc borate.[1] These are shown in Fig. 6.

Although absolute purity cannot be claimed for any of these compounds, from the examination of the emission bands of the "pure" and "activated" samples, it seems reasonable to assume that the wide diffuse bands are those due to the compounds themselves and not due to an undetected impurity. A more careful

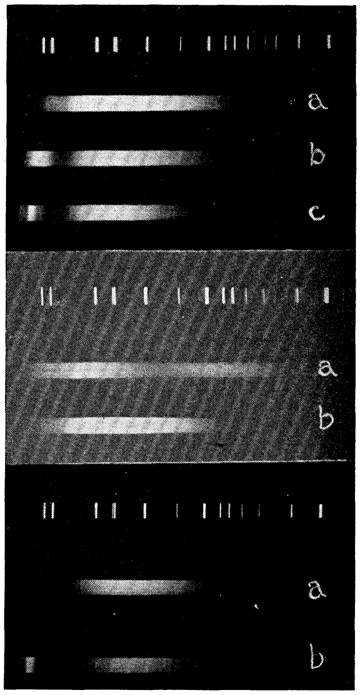

FIG. 6. Luminescence spectra of radium and barium compounds with comparison spectra of Hg arc. Upper panel: (a) pure $RaSO_4$; (b) $RaSO_4$+Mn; (c) $RaSO_4$+Sa. Middle panel: (a) $RaBr_2$; (b) $RaSO_4$. Lower panel: (a) pure $BaSO_4$; (b) $BaSO_4$+Sa.

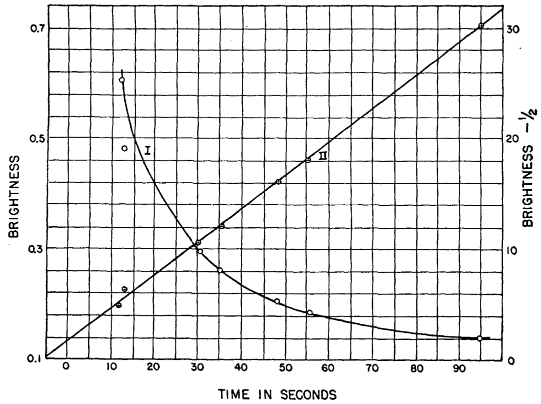

Fig. 7. Decay of phosphorescence of pure barium bromide.

examination of these bands and their dependence on the temperature of heat treatment seems desirable.

Ratio of Phosphorescence to Fluorescence

This ratio was determined for pure $BaBr_2$ by quickly removing the exciting source (the radium tube) and determining the decay rate of the residual brightness. This is shown in Fig. 7. Plotting the reciprocal of the square root of brightness against time gives a straight line indicating that the phosphorescence is a bimolecular reaction. From the intercept of this curve, the ratio of phosphorescence to fluorescence was found to be approximately equal to 5 percent.

Decay of Luminescence under Continuous Excitation

The decay of luminescence of pure radium sulphate was investigated. The decay was very rapid at the start, but soon became asymptotic with the time axis reaching a constant value and remaining so indefinitely. The decay curve is shown in Fig. 8. The curve is similar to those obtained for pure radium bromide by Rodman[5] and pure barium bromide obtained by Smith.[6] It is very complex. Factors such as decomposition of the compound, change in the absorption coefficient of the material due to discoloration as well as the destruction of the luminescent centers probably enter into it. It has not been possible to find a simple explanation for this decay. The compounds will invariably recover their full luminescence on being heated to the temperatures of maximum activation.

Discussion

When a crystal is irradiated by alpha-, beta- and gamma-rays from radium, as in the above experiments, the electrons can absorb sufficient energy to raise them to any unoccupied energy bands that may exist in the crystal, including the conduction bands (ionization). If these electrons could directly return to their normal levels, luminescence would result. The fact that only very faint luminescence can be obtained in unheated, pure crystals may mean one of two things: (*a*) that permissible and unoccupied energy bands do not exist in pure unheated crystals, (*b*) that such bands may exist but the conditions necessary for the direct return of the electrons to their normal levels, with emission of luminous energy, do not exist. The heating of the crystals to higher temperatures, and then cooling, apparently produces the structural changes necessary for luminescence. It is difficult to determine from these experiments the nature of this change. It cannot be due to a

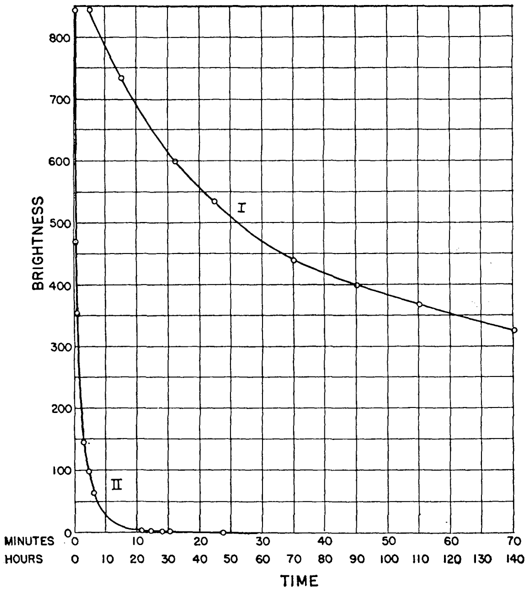

Fig. 8. Decay of luminescence of pure radium sulphate, Curve I time in minutes, Curve II time in hours.

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[5] J. Rodman, Phys. Rev. **23**, 478 (1924).

[6] L. E. Smith, Phys. Rev. **28**, 431 (1926).

chemical decomposition, as the compounds remain perfectly white after heating. However, there is distinct evidence of instability, indicated by the fact that heated radium bromide becomes almost black in time, while the unheated specimens show only a slight change in color.

Seitz[7] explains the luminescence of heat-treated pure ZnS as due to Zn atoms diffusing into the interstices of the crystal lattice and acting in the same way as impurity atoms. A similar displacement may be taking place in the case of barium compounds. This would explain the brightness-temperature curves if it be assumed that the number of displaced atoms depends on the temperature of heat treatment. It is still necessary, however, to explain why these give a much broader emission band than other impurity activators as shown in Fig. 6. A more thorough examination of the emission bands and their dependence on the temperature of heat treatment seems desirable.

The author wishes to acknowledge his indebtedness to Dr. G. P. Harnwell and Dr. F. Seitz for many valuable suggestions and criticisms. This research was aided by a grant from the Faculty Research Committee of the University of Pennsylvania and also by a grant from the American Philosophical Society which are hereby gratefully acknowledged.

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[7] F. Seitz, J. App. Phys. **10**, 479 (1939).

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The Band Spectrum of Antimony Chloride

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A band spectrum attributed to the molecule SbCl, in the region λλ4200–5600, has been excited by introducing $SbCl_3$ into active nitrogen. No other bands appeared in the range λ2000 to λ7000. The spectrum consists of bands showing pronounced progressions and degraded towards the red. They can be placed in two sub-systems of bands, designated as A_1 and A_2. Vibrational analysis shows that within experimental error the wave numbers of the heads of forty-one bands of $SbCl^{35}$ are represented by the formulas:

$$A_1 : \nu_1 = 22395 + 244.4u' - 2.28u'^2 - 368.0u'' + 0.84u''^2,$$
$$A_2 : \nu_2 = 25855 + 240.2u' - 2.19u'^2 - 370.0u'' + 1.00u''^2.$$

The chlorine isotope effect appears in 13 bands and is used to confirm the v', v'' designations. The analysis of the spectrum given here is somewhat different from that originally presented two years ago. Many more bands are here accounted for and identified. An attempt failed to produce a spectrum of AsCl by introducing $AsCl_3$ vapor into active nitrogen.

THE electron configurations of the lighter diatomic molecules have already been determined with a fair degree of certainty. Comparatively few measurements have thus far been made of the spectra of the heavy diatomic molecules. Spectra have been produced, however, for many of the diatomic halides of the elements in group IVb of the periodic table. For group Vb there are only the spectra due to SbF [1] and the four bismuth halides.[2] This experiment was undertaken to find out whether the same regularities exist for the halides of group Vb as have been shown to exist for group IVb.[3]

The arrangement of the apparatus and the methods employed for the excitation of the bands of antimony chloride are essentially the same as those originated by Strutt and Fowler[4] in their work with active nitrogen, and as further de-

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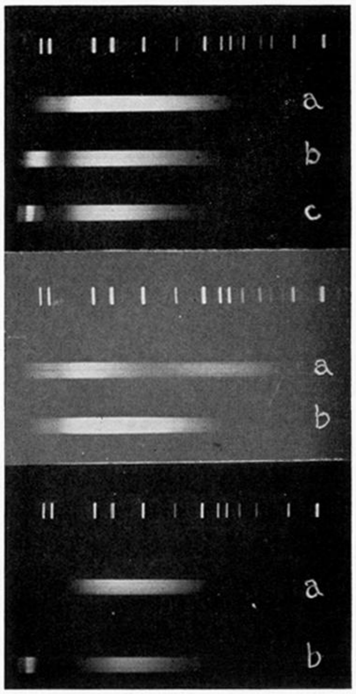
[1] G. D. Rochester, Phys. Rev. **51**, 486 (1937).

[2] F. Morgan, Phys. Rev. **49**, 41 (1936).

[3] W. Jevons, L. A. Bashford and H. V. A. Briscoe, Proc. Phys. Soc. **49**, 532 and 537 (1937); W. Jevons and L. A. Bashford, Proc. Phys. Soc. **49**, 554 (1937).

[4] R. J. Strutt and A. Fowler, Proc. Roy. Soc. **A86**, 105 (1911).



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