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LUMINESCENCE EXCITED BY X-RAYS IN COLLOIDAL ALKALINE EARTH SALTS*

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Abstract

The gelatinous precipitates of calcium, strontium and barium fluoride are positive colloids. The precipitates formed in the presence of an excess of calcium, strontium or barium ions luminesce in x-rays. The intensity of luminescence increases after the precipitate has been brought to red heat. The salts that are precipitated in the presence of excess fluoride do not luminesce in x-rays. The positively charged fluorides are changed into negative colloids by washing in dilute alkali; this causes the disappearance of the luminescence. Washing with dilute acid or distilled water is without effect. Colloidal barium sulphate shows a similar behaviour. Calcium tungstate and strontium tungstate are negative colloids; the precipitates formed in the presence of excess tungstate ions fluoresce brightly in x-rays. The precipitates formed in the presence of excess calcium or strontium ions fluoresce very faintly. A table is given showing the extent of the luminescent bands into the ultra-violet. Fluorides that have been heated in a hydrogen atmosphere show a dark discoloration and do not luminesce in x-rays. The presence of impurities diminishes the luminescence of colloidal precipitates. The alkaline earth chlorides and phosphates, calcium and strontium sulphate, and barium tungstate formed only crystalline precipitates that did not luminesce in x-rays. The hypothesis is made that the luminescence of colloidal precipitates is due to a thin layer of metallic oxide which is formed from the double layer of ions that is adsorbed on the surface of the colloidal particles.

IN THE course of a study of ultra-violet flurescence it became necessary for us to prepare calcium fluoride that did not show any luminescence when exposed to x-rays. Urbain and Bruninghaus[1] state that perfectly pure compounds do not phosphoresce. Pringsheim[2] thinks it very probable that chemically pure calcium fluoride does not fluoresce, but does not consider this to have been proved. Gyemant[3] observes that chemically pure calcium tungstate shows luminescence and thinks that the crystalline state is necessary for its appearance. Baly[4] also stresses the importance of the crystalline state and thinks that Urbain's generalisation about the importance of impurities was due to the fact that he worked with oxides of the rare earths, that are amorphous in the pure state. Perrine[5] observed fluorescence during the excitation by x-rays of chemically pure barium sulphate and calcium tungstate amongst others.

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[1] Urbain and Bruninghaus, Ann. Chim. et Phys. **18**, 293 (1909).

[2] Pringsheim, Fluorescenz und Phosphorescenz im Lichte der neueren Atomtheorie, Berlin, 1923.

[3] Gyemant, Chemiker Zeitung, **49**, 493 (1925).

[4] Baly, Spectroscopy, Vol. II, London, 1927.

[5] Perrine, Phys. Rev. **22**, 48 (1923).

We prepared calcium fluoride by precipitating a solution of c.p. calcium chloride with c.p. potassium fluoride. When 5 mols $CaCl_2$ are mixed with one mol KF the calcium fluoride forms a gelatinous precipitate. The dried precipitate which has been centrifuged and washed repeatedly shows a faint greenish fluorescence when exposed to x-rays. This fluorescence is very much brighter when the calcium fluoride has been brought to red heat for one minute before being exposed. The luminescence persists for several hours after sufficient excitation; after its extinction a renewed light emission can be caused by heating. In other words, the precipitate of calcium fluoride behaves in every respect like a phosphor.

When an excess of potassium fluoride (10 mols KF to one mol $CaCl_2$) is used, the precipitate is also gelatinous, but does not show any luminescence in x-rays either before or after heating.

The spectrum of the fluorescence light was photographed on panchromatic plates with a Hilger quartz spectrograph that was shielded from the x-rays. The substance to be studied was contained in a cell of cellophane which is transparent to ultra-violet light and does not fluoresce in x-rays. A Coolidge universal tube was used with a potential of 80 kilovolts and a current of 3 milliamperes. The tube was enclosed in a leaden box and immersed in water-cooled oil as prolonged exposures were needed to obtain the spectrograms. The target distance was 25 cm. A point-plane spark-gap and circuit-breaker were used to protect the tube against reversal of polarity and overload. Under these conditions the x-ray machine could be left running continuously for 24 hours without requiring any attention.

TABLE I. *Wave-lengths of fluorescence bands*

Substance examined	Wave-length of band of fluorescent light	Duration of exposure
Calcium fluoride (excess calcium)	700–270 $m\mu$	72 hours
Calcium fluoride (excess fluorine)	—	72
Calcium fluoride (excess calcium and gadolinium)	700–320	72
Barium fluoride (excess barium)	700–320	72
Barium fluoride (excess fluorine)	—	72
Strontium fluoride (excess strontium)	700–330	72
Strontium fluoride (excess fluorine)	—	72
Barium sulphate (excess barium)	700–330	72
Barium sulphate (excess sulphate)	—	72
Calcium tungstate (excess tungstate)	510–370	24
Calcium tungstate (excess calcium)	500–390	72
Strontium tungstate (excess tungstate)	700–310	72
Strontium tungstate (excess strontium)	—	72

The fluorescence spectra of all the colloidal precipitates that were studied consisted of diffuse bands; their extent and the time of exposure are given in Table I.

The precipitates of strontium fluoride and barium fluoride are colloidal and their luminescence is similar to that of calcium fluoride; only the salts that are prepared in the presence of excess strontium or barium ions show phosphorescence when exposed to x-rays.

Calcium sulphate, strontium sulphate and barium sulphate that were prepared by precipitating solutions of the alkaline earth salts with sulphuric acid are crystalline and do not show any luminescence in x-rays, no matter in what proportion the ingredients are mixed. Von Weimarn[6] described a method by which barium sulphate is precipitated as a jelly; it consists in precipitating a 3–7 mol solution of barium thiocyanate with manganese sulphate. We prepared a colloidal precipitate of barium sulphate in this manner, but used ammonium sulphate instead of manganese sulphate, thus avoiding the presence of all metals except barium. This precipitate that was prepared in the presence of a large excess of barium ions phosphoresced in x-rays.

The chlorides and phosphates were always precipitated in the crystalline state in our experiments and do not show any luminescence in x-rays.

Calcium tungstate forms a colloidal precipitate which phosphoresces in x-rays. Its luminescence offers an important difference from that of calcium fluoride in that it depends upon the presence of an excess of tungstate ions instead of calcium ions. The precipitate that is formed in the presence of an excess of tungstate ions phosphoresces brightly when exposed to x-rays after having been heated. The intensity of its fluorescence is the same as that of the commercial x-ray intensifying screens, from which it only differs by the much slower rate of decay of its phosphorescence. Calcium tungstate prepared with an excess of calcium ions present shows only a very faint luminescence.

Strontium tungstate behaves similarly to calcium tungstate but the intensity of the luminescence of the salt prepared with excess tungstate ions present is much less than that of the corresponding calcium salt. The intensity of the luminescence of the salts prepared with excess strontium or calcium ions is approximately the same and very faint.

The precipitate of barium tungstate was crystalline in all our experiments; it does not show any luminescence in x-rays.

Calcium carbonate prepared by precipitating a solution of calcium hydroxide with CO_2 phosphoresces in x-rays after it has been heated. This phosphorescence is apparently due to the presence of calcium oxide as the salt loses its capacity for luminescence in x-rays after it has been exposed to the air for some time. This made it impossible to obtain a spectrogram because the cellophane cell is not airtight; quartz cells cannot be used in these experiments as all samples of fused quartz that we examined fluoresce in x-rays.

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[6] Von Weimarn, Die Allgemeinheit des Kolloidzustandes, Dresden, 1925.

Calcium oxide prepared from freshly precipitated calcium carbonate fluoresces in x-rays; the intensity of its luminescence is less than that of calcium fluoride that is prepared in the presence of excess calcium ions.

It is a surprising fact that only those alkaline earth salts that were precipitated in the colloidal state show phosphorescence in x-rays, and that the appearance of luminescence depends upon the relative concentration of the precipitating ions.

Fajans and Frankenburger[7] have observed a similar relation between optical phenomena and the colloidal state in the case of silver bromide. The bromide precipitated from a solution containing excess Ag ions is a positive colloid and is sensitive to visible light; the limit of its sensitiveness is probably in the infra-red. The bromide precipitated from a solution containing excess bromine ions is a negative colloid and is only sensitive to light of wavelengths smaller than 435 mμ. They could demonstrate analytically that the positive colloid contained an excess of silver over the stochiometric proportions.

Calcium fluoride behaves differently in one respect: both the salt that is precipitated from a solution containing an excess of calcium ions and that which is precipitated from a solution with excess fluorine ions are positive colloids and go to the cathode in an electrophoretic apparatus. All precipitates of calcium tungstate on the other hand are negative colloids.

The colloidal state is due to an electric charge on the colloidal particles which keeps them apart. It is generally believed[8] that this charge is due to the existence of a double layer of ions. In the case of a positive colloid the inner layer consists of positive ions that are adsorbed on the surface of the particle; the outer layer consists of a region where the negative ions of the surrounding fluid are more concentrated to neutralize the charge resulting from the adsorbed ions. The ions that are adsorbed on the particles of the precipitate that was formed by adding one mol KF to five mols $CaCl_2$ may be Ca, K or H. In the precipitate formed by mixing one mol $CaCl_2$ with ten mols KF, only K or H can have been adsorbed. Since only the former shows luminscence, it is possible that this is due to the adsorbed calcium ions.

This supposition is confirmed by the effect of washing the colloidal precipitate in dilute acid or alkali. Calcium fluoride particles that are suspended in water or in dilute acid go to the cathode; the same particles go to the anode when they are suspended in normal NaOH. According to the theory outlined above, suspension in NaOH solution must involve the loss of the layer of adsorbed calcium ions. And indeed, if calcium fluoride that has been freshly precipitated from a solution with excess calcium ions is suspended in normal NaOH and then washed with distilled water, it loses its capacity for luminescence in x-rays. Washing with distilled water alone or with normal hydrochloric acid is without effect on the luminescence.

The second, outer layer that surrounds the particle with the adsorbed calcium ions consists of a zone where the negative ions of the surrounding

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[7] Fajans and Frankenburger, Zeits. f. Physik. Chemie, **55**, 255 and 273 (1923).

[8] Bogue, Colloidal Behavior, New York, 1924.

fluid are more concentrated as a result of electrostatic attraction. After the precipitate has been washed repeatedly, these negative ions must be mainly OH ions. The effect of heating the precipitate to red heat will be to transform this double layer of Ca and OH ions into a thin film of calcium oxide. We are inclined to ascribe the luminescence of colloidal salts to this thin oxide film. Nichols and Wilber[9] have observed fluorescence in thin films of calcium, strontium and barium oxide amongst others. The films were prepared by sublimation in the electric arc and fluoresced when bombarded by cathode rays. They also state that this fluorescence does not depend upon the presence of an admixture of foreign material. The phosphorescence of the thin films of oxide surrounding the colloidal particles is entirely similar to the phenomenon described by Nichols and Wilber. The only difference is that our colloidal salts phosphoresce while the thin films of Nichols and Wilber only fluoresce. The electron that is emitted from the CaO molecule under the influence of the cathode rays returns immediately with light emission in the case of the thin films described by Nichols and Wilber. In the case of our colloidal precipitates the emitted electron may apparently be captured by the calcium fluoride particle and return after a longer or shorter interval and so cause the appearance of phosphorescence.

It might be supposed that the effect of heating the calcium fluoride is simply to transform the colloidal precipitate into the crystalline state, and that the excess Ca ions play the role of the impurity postulated by Urbain for the appearance of phosphorescence. However, if we moisten a non-fluorescent sample of calcium fluoride with a few drops of a dilute solution of calcium choloride or calcium hydroxide, dry it and bring it to red heat, it does not acquire the faculty of fluorescing in x-rays. If we treat a phosphorescent sample of calcium fluoride in the same way, we cause a considerable diminution of its light emission or even its entire disappearance. Other impurities than calcium salts have the same effect on the light emission. Urbain[10] showed that the ultra-violet fluorescence of some natural fluorides is due to the presence of gadolinium. If we prepare a fluoride by precipitating a solution containing five mols calcium chloride and one mol gadolinium nitrate with one mol KF, the precipitate shows the same type of fluorescence as that prepared without gadolinium but of much lower intensity.*

When a sample of luminescent calcium fluoride is brought to red heat in a hydrogen atmosphere, it turns dark grey and loses its capacity for luminescence in x-rays. The same change of color and partial loss of the capacity for luminescence in x-rays takes place after prolonged exposition to x-rays. Heating in the air restores in both cases the white color and the original intensity of luminescence. If the discoloration is caused by the formation of metallic calcium as seems likely, this offers another proof that the presence of calcium oxide is the cause of the light emission.

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* We wish to express our thanks to Professor B. S. Hopkins of the University of Illinois, who so kindly put the gadolinium that was used in this experiment at our disposal.

[9] Nichols and Wilber, Phys. Rev. **17,** 107 (1921).

[10] Urbain, Ann. d. Chim. et Phys., **18,** 327 (1909).

The calcium ions are very firmly bound to the colloidal calcium fluoride particles, and no amount of washing with distilled water can remove them. Barium sulphate presents an interesting difference from calcium fluoride in this respect. If barium sulphate that has been freshly precipitated in the colloidal state from barium thiocyanate solution is washed and centrifuged three times with large quantities of distilled water, the dried and heated precipitate phosphoresces; if the same precipitate is washed ten times it does not show any luminescence in x-rays. The capacity for luminescence cannot be restored by moistening the precipitate with a few drops of dilute barium thiocyanate solution. The presence of a thin film of barium oxide is again necessary for the appearance of luminescence. The barium ions are not as firmly attached to the barium sulphate as the calcium ions are to the calcium fluoride particles, which explains why special precautions have to be taken to obtain colloidal barium sulphate.

The luminescent qualities of calcium fluoride that has been brought to red heat are not modified by subsequent exposure to air or water although calcium oxide under the same circumstances is changed into non-luminescent calcium hydroxide. The adsorption on the surface of the calcium fluoride particles has apparently not only modified the optical but also the chemical properties of the oxide, unless we want to assume that the adsorbed calcium oxide film has formed a chemical combination with the calcium fluoride particle; the distinction seems however immaterial.

Calcium tungstate is a negative colloid and we must consider the adsorbed tungstate ions as responsible for its luminescence. The precipitate that is formed in the presence of excess calcium ions shows only a faint luminescence of the same spectral character as that of the precipitate with excess tungstate ions. The presence of impurities or moistening the precipitate with dilute solutions of tungsten compounds again diminishes the intensity of the luminescence. None of it is apparently due to calcium ions, but since the precipitate that is formed in the presence of excess calcium ions also phosphoresces, we must assume either that pure calcium tungstate phosphoresces or that the surface of calcium tungstate particles always contains an excess of tungstate ions. The latter supposition is supported by the fact that calcium tungstate is always a negative colloid irrespective of its mode of preparation. On this supposition we ought to expect that calcium fluoride that has been precipitated from a solution with excess fluorine ions ought also to show some luminescence, because it has the same positive charge as the phosphorescent calcium fluoride. This luminescence is perhaps too faint to be observed, as the light emission of all fluorides is much less than that of calcium tungstate. It is impossible to decide between these two possibilities by washing the calcium tungstate with acid, which should remove the excess tungstate ions in the same way as washing with alkali removes the excess calcium ions from calcium fluoride, because calcium tungstate is chemically changed by acids.

SUMMARY

1. Freshly precipitated calcium fluoride, strontium fluoride, barium fluoride, barium sulphate, calcium tungstate and barium tungstate phosphoresce on exposure to x-rays. This phosphorescence is much brighter when the precipitate has been brought previously to red heat for one minute.

2. The precipitated fluorides and sulphates are positive colloids. Their luminescence depends upon the presence of an excess of calcium, strontium or barium ions in the precipitating solution.

3. Calcium tungstate and barium tungstate are negative colloids. Their luminescence depends upon the presence of an excess of tungstate ions in the precipitating solution.

4. No luminescence on exposure to x-rays could be demonstrated in crystalline precipitates of alkaline earth salts.

5. The presence of a thin film of oxide on the surface of the heated colloidal particles is suggested as responsible for their luminescence.

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