A SPECTROSCOPIC STUDY OF THE CATHODO-LUMINESCENCE OF FLUORITE

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Abstract

Spectra of the cathodo-luminescence of five samples of fluorite.—In the case of natural fluorite, the spectra excited consist of broad diffuse bands upon which are superimposed sharp bands. *The effect of heating to 600°C* before bombardment is to intensify the sharp bands and to weaken the diffuse ones. *The effect of fusion in an oxidizing flame* is much more radical, the color is changed and many new narrow bands are emitted. The wave-lengths as determined photographically and visually are given in tables. Comparison with the results of Urbain for cathodo-luminescence spectra of small percentages of rare earths in CaO and in CaF_2 shows that the bands observed are due to rare earth impurities the most prevalent and conspicuous being samarium, dysprosium, europium, gadolinium and terbium. The fusion changes the fluoride to the oxide, at least on the surface. The sharpness of the bands and the dependence of the spectra upon the diluent materials is explained if we assume that the rare earth atoms enter into the crystal lattice and emit light under constraint by the neighboring atoms.

FLUORITE crystals may be excited to luminescence, as is well known, by various forms of energy such as heat, light, ultra-violet radiations, cathode rays, x-rays and radium. The luminescence due to cathode rays is characterized by a spectrum consisting of broad, diffuse bands upon which are superimposed, in the case of crystals from certain localities, sharp bands some of which are nearly as narrow as lines of a gaseous spectrum. The source of these lines has been the subject of much investigation and some disagreement. Urbain,[1] ascribed these lines to the presence of rare earth impurities in quantities too small for detection by chemical analysis. Morse[2] was unable to prove that the lines observed were due to rare earths, but Tanaka,[3] has identified certain rare earths as the active agents.

The work here described was undertaken with the hope of getting further evidence as to the source of the sharp lines in the luminescence spectra of fluorites. The experimental difficulties involved in the study of the natural crystals are great because the lines are very dim and the change of the surfaces of the crystals under cathode ray bombardment makes necessary the exposure of a number of fresh surfaces for a

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[1] Urbain, Comptes Rendus **143,** 825 (1906); Ann. de Chemie et de Phys. (8), **18,** 256 (1909)

[2] Morse, Proc. Am. Acad. **41, 587** (1905-06); **43,** 1 (1907-08)

[3] Tanaka, J. Opt. Soc. Amer. **8,** 501 (1924)

single photograph. Since it is well known that heat treatment often has the effect of increasing the intensity of luminescence, it seemed possible that subjection of the fluorites to a high temperature before exposure to cathode rays might bring out the lines more strongly. The experiments here described show that by subjecting the fluorites to a temperature high enough to fuse them, very sharp line spectra of much greater intensity than any observed with the unheated specimens may be brought out, thus making visual and photographic observations much easier. The results obtained from the study of such spectra verify the conclusion of Urbain that the lines in the luminescence spectra of fluorites are due to rare earth impurities.

From a large number of fluorites occurring in widely different localities and showing a great variety of colors and intensities of luminescence, a few were selected in which sharp, line-like bands were superimposed upon the characteristic broad bands of the cathode ray spectra. Results are here given of observations upon the following varieties:

Specimen 1, blue-green fluorite from Weardale, England;
" 2, purple fluorite from Weardale, England;
" 3, yellow fluorite from Scoredale, England;
" 4, clear green fluorite from New South Wales;
" 5, chlorophane from Virginia Courthouse.

Apparatus

A part of the apparatus used for the study of the cathode ray spectra is shown in Fig. 1. The crystal under observation was mounted in a tube *T* (with a ground glass joint *B*) on an aluminum support so placed that the rays struck the specimen *C* at an angle of about 45 degrees. For the study of the ultra-violet spectra, the tube containing the specimen was made of Pyrex glass with a quartz window in front of the specimen *C*, and a Hilger quartz spectrograph was used. For the study of the visible spectra, a Hilger spectrograph or spectroscope of the constant deviation type was placed with its collimator slit at *S*. The vacuum in the cathode ray tube was maintained by an oil pump kept running continuously because the specimens gave off gas upon bombardment. A Wappler x-ray machine was used as a source of excitation, the voltage varying with the state of the vacuum up to a maximum measured by an equivalent spark gap of a little over 2 cm. Ilford Special Rapid Panchromatic plates were used for work in the visible region and Seed 30 plates for work in the ultra-violet.

Effect of Heat Treatment

Specimens of fluorite were heated in an electric resistance furnace for periods of from one to three hours to temperatures varying from 300°

to 600°C. Such treatment, as is well known, takes out all the natural color and usually causes the larger crystal masses to go to pieces or to become cracked and opaque. A study of the specimens under cathode ray bombardment shows that the luminescence very often has its color somewhat changed by this process of heating so that the red end of the spectrum is more prominent than it was before, and, in general, the period of phosphorescence is lengthened. The intensity of the line-like bands is increased and that of the diffuse bands decreased by the heating, but the positions of the lines are not changed.

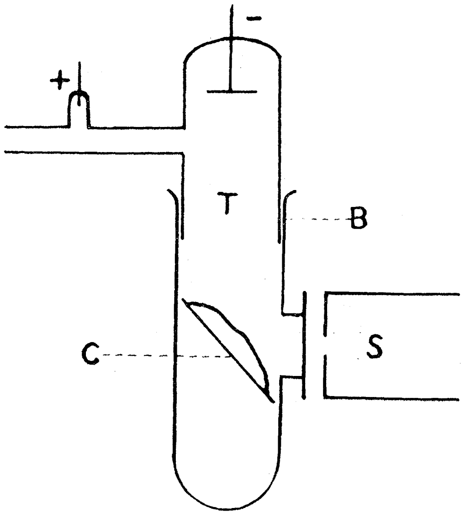

Fig. 1. Diagram of tube.

Specimens of fluorite similar to those heated in the resistance furnace were heated by playing upon them an oxy-hydrogen or oxy-gas flame until fusion took place, at a temperature between 1100° and 1200° C as indicated by an optical pyrometer. The cathodo-luminescence of the fused specimens was quite different from that of the unfused, often changing from blue or green to orange or red. The spectra are characterized by very sharp lines of much greater intensity, more numerous and most of them with different wave-lengths from those observed with the natural crystals.

The character and intensity of the luminescence are greatly influenced by the conditions under which fusion takes place, such as the relative pressures of oxygen and hydrogen. It appears that the radical change brought about in the luminescence by fusion is due to the fact that, during the heating, a part of the calcium fluoride, at least a thin surface layer is changed to calcium oxide, a conclusion verified by a chemical analysis kindly made by Dr. Kilpatrick of the Department of Chemistry, Vassar College. In fact by powdering the natural material and heating it in an ordinary air-gas blast until the surface becomes oxidized, exactly the same changes can be produced which are brought about by fusion. A very satisfactory way of preparing the material for study in the cathode ray tube is to fuse the powdered fluorite in an oxy-gas flame and then to heat the surface further in an air-gas blast until more complete oxidation of the surface had taken place.

From observations made upon these oxides, it appears that the relative intensities of lines and continuous bands depend upon the voltage applied to the tube, determined by the state of the vacuum, and upon the temperature of the specimen. In general, the lines come out most strongly and sharply at the high voltages, and the bands are most conspicuous at low voltages with higher current values. There is some evidence that the lines in the red end of the spectra are brought out by lower voltages than those of shorter wave-length and that raising the voltage applied to the tube pushes the continuous bands in the ultra-violet to shorter wave-lengths, but it is very difficult to tell just how much of the change is due to change in temperature under cathode-ray bombardment, and further experiments in which more accurate control of conditions is possible are necessary before any conclusions may be drawn.

Photo-Electric Measurements of Spectrograms

In order to get some quantitative idea of the changes in relative intensity of different parts of the spectra brought about by fusion, some of the photographs of the spectra obtained were measured by means of a photo-electric cell apparatus used by Perrine[4] and described briefly by Boardman.[5] Light from a 100-watt lamp was brought to a focus upon a slit 2 mm by .25 mm, and after passing through a section 2×.25 mmof the photographic plate, entered a Kunz photo-electric cell, connected in series with a Leeds and Northrup Type C galvanometer. Samples of the curves obtained are shown in Fig. 2. Curve A was obtained from a natural specimen and shows a broad luminescence. Curve B shows the corresponding spectrum of the fused specimen and indicates that the intensity of the broad band is relatively greatly reduced, while numerous narrow bands appear.

Identification of Lines

Urbain gives data with regard to the spectra obtained by placing very small amounts of various rare earths in calcium fluorite, calcium oxide,

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[4] J. O. Perrine, Phys. Rev. **22,** 48 (1923); J. Opt. Soc. Amer. **8,** 321 (1924)

[5] L. J. Boardman, Phys. Rev. **20,** 552 (1922)

and calcium sulfate. The same rare earth produced a different spectrum in each of these different substances.

In order to test for rare earth impurities, specimen 1 was converted into calcium oxide by the method of heating described above, and some of the oxide was chemically converted into calcium sulfate. The spectra of these substances were observed visually and photographically and the results were compared with the spectra given by Urbain. The spectrum of the natural crystal (Fig. 3, spectrum 1) showed only a few lines and those were Urbain's strongest lines for samarium in calcium fluoride. The sulfate (Fig. 3, spectrum 3) showed a spectrum almost entirely due to dysprosium, and the oxide (Fig. 3, spectrum 4) gave a spectrum very rich in sharp, bright lines the most conspicuous of which in the visible region were due to samarium. Dysprosium was also present as shown especially by the strong citron band of Urbain, europium lines came out weakly, and terbium and gadolinium lines were very conspicuous in the ultra-violet.

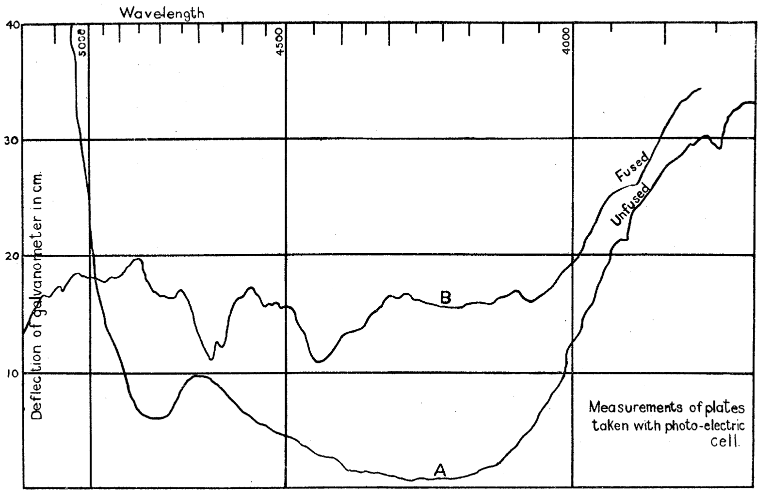

Fig. 2. Transmission of spectrograms as a function of wave-length. A, luminescence of natural specimen; B, fused specimen.

Spectra of Fused and Oxidized Specimens

Since the lines in the fused and oxidized specimens are more numerous and are also very much brighter and more easily observed than those in the natural fluorites, the cathodo-luminescence spectra of the oxides prepared from different specimens were examined visually and photographically for the purpose of detecting rare earth impurities. Table I gives visual observations of the spectra of the five fused fluorites and the corresponding positions of crests observed by Urbain in the cathode ray

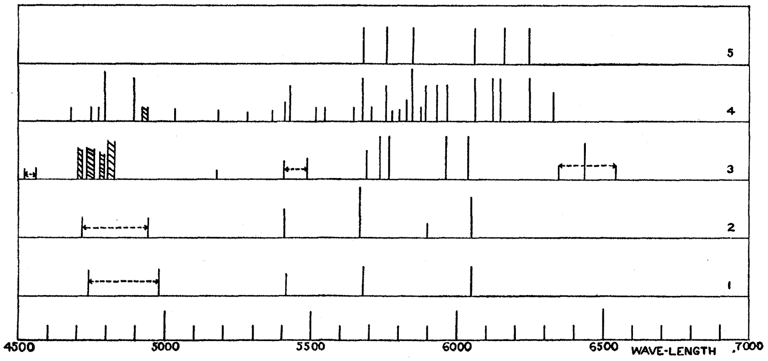

Fig. 3. Position and relative intensity of lines of various luminescence spectra.
Dotted lines indicate diffuse bands.
Spectrum 1, natural fluorite
Spectrum 2, fluorite heated to 600°C
Spectrum 3, calcium sulfate made from the fluorite
Spectrum 4, calcium oxide from fluorite
Spectrum 5, same as 4 diluted with CaO

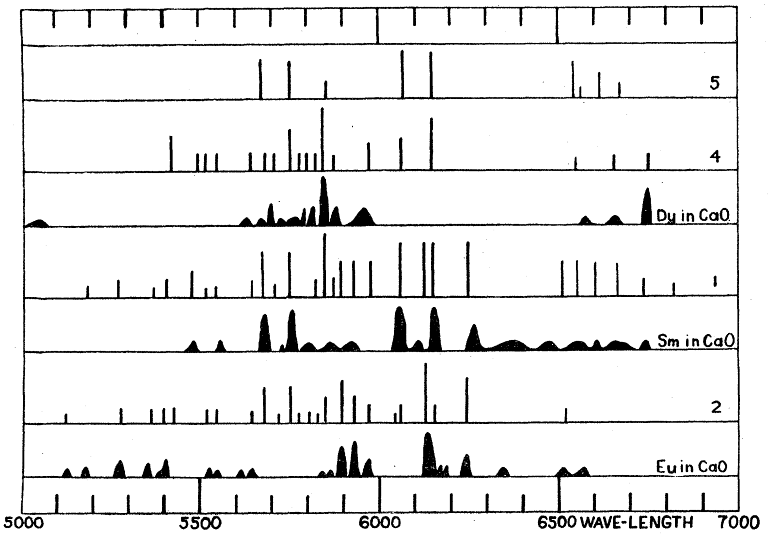

Fig. 4. Comparison of prominent bands in spectra of fused fluorites Nos. 1, 2, 4, 5, with maxima of Urbain, Eu in CaO, Sm in CaO and Dy in CaO.

luminescence of rare earths in calcium oxide. Fig. 4 shows the same comparison graphically; the relative intensities of the narrow bands observed in specimens 1, 2, 4, and 5 are indicated by lines of different lengths;

TABLE I

Visual observations of positions of narrow bands in the long wave-length end of the spectra of fused fluorites, and corresponding maxima of Urbain for rare earths in CaO.*

vs, *s*, *m*, and *d* indicate relative intensities to be very strong, strong, medium, and dim; *h* indicates that the band is hazy or diffuse; all wave-lengths given in A. U.

Specimen of fluorite					Rare earths in CaO
No. 1	No. 2	No. 3	No. 4	No. 5	Data from Urbain
		6763 *vvd*	6759 *vd*		
			6754 *d*		*Dy* 675_0 *s*
6740 *d, h*					*Sm* 674_0 *m*
		6675 *vvd*		6670 *d*	*Dy* 667_0 *vd, h*
6665 *m*					*Sm* 666_0 *m, h*
6601 *m*					*Sm* 6605 *s*
		6612 *d*		6617 *m*	
		6572 *d*		6568 *vd*	*Eu* 657_0 *vd, h*
6556 *m*			6550 *vd*	6549 *m*	*Dy* 6545 *vd*
					Sm 654_0 *m, h*
6511 *m*					*Eu* 651_0 *d, h*
	6522 *d, h*	6521 *m*			
6251 *s*	6250 *vs*	6253 *s*			*Sm* 6265 *vs*
					Eu 6245 *s*
6156 *s*	6159 *vd*	6156 *m*		6153 *s*	*Eu* 6155 *m*
6150 *s*			6150 *vs*		*Sm* 6150 *vs*
6129 *s*	6129 *vvs*	6129 *s*			*Eu* 6128 *vs*
6063 *vd*	6066 *vd*	6063 *m*	6062 *s*	6071 *s*	*Pr* 6065 *vs*
					Sm 6052 *vs*
	6045 *vvd*				*Pr* 6045 *s*
5971 *d*	5974 *m*	5979 *m*	5977 *h*		*Eu* 597_0 *m*
5931 *d*	5932 *m*	5935 *m*			*Eu* 593_0 *vs*
5898 *d*	5900 *s*	5900 *m*			*Eu* 5895 *ss*
					Tb 5897 *vs*
5876 *d*		5878 *d*	5880 *vd*		*Tb* 5878 *s*
					Dy 5877 *m, h*
5851 *vvs*	5851 *d*	5850 *vvs*	5850 *vvs*		*Dy* 5848 *vvs*
				5859 *m*	*Sm* 5865 *d, h*
5833 *d*	5834 *vvd*	5833 *vd*	5829 *vd*		*Dy* 583_0 *vs*
5805 *d*	5808 *vvd*	5805 *vd*	5802 *vd*		*Dy* 5805 *m*
5783 *vd*	5779 *vvd*	5782 *vvd*	5780 *vd*		*Dy* 5785 *m*
					Dy 5775 *m*
				5764 *m*	*Sm* 5762 *vs*
					Dy 5763 *m*
5756 *m, h*	5757 *m*	5757 *m, h*	5756 *s*		*Dy* 5752 *m*
	5721 *vd*				*Sm* 5725 ?
					Tb 5717 *d*
5714 *d*			5712 *vd*		*Dy* 5708 *vs*
5683 *d*	5683 *m, h*	5686 *m, h*	5684 *m*	5681 *vd*	*Sm* 5683 *vs*
5650 *d, h*	5645 *d, h*				*Eu* 5645 *d*
5551 *d, h*	5548 *vvd*		5549 *d, h*		*Tb* 5550 *s, h*
					Eu 5545 *d*
5516 *d, h*	5521 *d, h*		5519 *d, h*		*Tb* 5521 *s, h*
			5497 *d, h*		*Tb* 5495 *vs, h*
5429 *m*			5430 *s*		*Tb* 5438 *s, h*
					Tb 5425 *s, h*
5411 *d, h*	5412 *vvd*				*Tb* 540_0-539_0 max. of band
	5401 *vvd*				*Eu* 5401 *vs*
5373 *vd*	5371 *m, h*				*Eu* 5365 *m*
	5284 *vvd*				*Eu* 528_0 *m*
5181 *vvd*					*Eu* 518_0 *m, h*
5036 *vvd*			5025	5010	*Dy* $5063–500_0$ *d*
			to	to	*Dy* $495_0–491_0$ *m,h*
			4899	4866	*Dy* $490_0–4882$ *s,h*

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* Wave-lengths longer than 6500 were obtained from photographic plates.

the solid black diagrams given for comparison indicate the bands due to europium, samarium, and dysprosium in calcium oxide as represented by Urbain. The correspondence between the maxima of Urbain and the bands in the fused fluorites is very striking.

Table II gives a comparison of the positions of the bands in specimen 4 determined photographically, with the maxima of bands observed by Urbain in the spectra of rare earths in calcium oxide. It will be observed that the dysprosium, terbium, and gadolinium bands are very prominent in this specimen. The bands on the photographic plates were extremely sharp and narrow, many of them no wider than the lines of the cadmium spark used for comparison. They appear to be narrower than those of Urbain.

The spectroscopic observations on the various specimens lead to the following conclusions.

Specimen 1. [Often occurring in good, clear crystals having a green transmission color and blue photo-luminescence giving the material a blue-green appearance by daylight.] Spectrum lines from natural crystal principally due to samarium. The oxidized specimen shows strongest lines due to samarium and gadolinium. Terbium, dysprosium, and europium are also present.

Specimen 2. [Sometimes occurring in clear, purple crystals but more often in imperfect, purplish-white masses.] The strongest lines in the fused specimen are due to europium and the relative brightness of these lines indicates, according to Urbain,[6] the presence of a relatively large amount. Samarium, dysprosium and gadolinium lines are also present but these are much less prominent.

Specimen 3. [Found in clear, relatively good yellow crystals.] Spectrum of the oxide is similar to that of specimen 1 with a difference in the relative intensities of the lines. The strong "citron line" of dysprosium is by far the most conspicuous. Other lines show the presence of samarium, europium, gadolinium and terbium.

Specimen 4. [A clear, green specimen from a monozite-bearing lode in Torrington, New South Wales.] Natural specimen shows conspicuous bands indicating the presence of terbium, dysprosium, erbium, gadolinium, and samarium. In the fused specimen, lines characteristic of these elements with the exception of erbium and with the addition of traces of europium, are present. The lines characteristic of gadolinium in calcium oxide and of gadolinium in calcium fluorite are present in the fused specimen indicating that both the oxide and fluoride must be

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[6] Kayser, Spectroscopie, Vol. IV, p. 811

present in the fused specimen. The most conspicuous rare earth present is terbium.

TABLE II

Photographic observations of positions of narrow bands in the spectrum of fused fluorite No. 4 and corresponding maxima obtained by Urbain from rare earths in calcium oxide.

Fluorite specimen 4	Rare earths in CaO Data from Urbain
5683 *s*	*Dy* 569_0 *d, h*
	Tb 5687 to 5602 *h*
5654 *d*	*Dy* 566_0 to 563_0 *d, h*
5560 *m*	*Tb* 5570 middle of band
	Tb 5550 *vs, h*
5528 *m*	*Tb* 5521 *vs, h*
5506 *m*	*Tb* 5508 *vs*
5437 *s*	*Tb* 5438 *s, h*
5409 *vd*	*Tb* 540_0-539_0 max. of band
5054 *vd*	*Dy* 5063 to 500_0 *d, h*
5035 *vd*	*Dy* 503_0 *d, h*
4998 *d*	
4976 *d*	
4946 *m*	*Dy* 4955 to 491_0*m*
4927 *d,h*	
4901 *s*	*Dy* 490_0 to 4882
	Dy 486_0 to 4825
4850 *m,br,h*	*Tb* 4855 *vs*
4832 *d*	
4825 *s*	*Tb* 4825 *m, h.*
4800 *s*	*Dy* 4797 *s, h*
4787 *vd*	*Tb* 4785 to 4730 *d, h*
4780 *m*	
4767 *m*	*Dy* 477_0 *d*
4746 *d*	*Dy* 4748 *m, h*
4719 *d*	
4685 *d,h,br*	*Dy* 469_0 to 4665 *h*
4646 *d*	
4624 *vd*	*Dy* 4628 *h*
4616 to 4568	*Tb* 462_0 to 457_0 *m*
4600 *d,h*	*Eu* 456_0 indistinct maximum
4585 *d,h*	
4545 *m*	*Dy* 454_0 *m, h*
4499 *m*	*Eu* 449_0 *vs, h*
4481 *m*	
4472 *d*	*Tb* 4472 *vs*
	Eu 4466 *vs, h*
4457 *vd*	*Tb* 4455 *vs*
4440 *vd*	*Tb* 444_0 *m, h*
4430 *vd*	
4408 *m*	*Tb* 441_0 *m, h*
4393 *s*	*Tb* 4395 *s*
4378 *s*	*Tb* 437_0 *vs, h*
4368 *s*	*Tb* 435_0 *s*
4344 *s*	*Tb* 434_0 *d, h*
4336 *vvd*	*Eu* 433_0 *vs, h*
4328 *vvd*	*Eu* 4315 *m*
4307 *vd*	*Tb* 430_0 *vd, h*
4274 *vvd*	*Eu* 4275 *m, h*
4223 *m*	*Tb* 422_0 *m, n*
4213 *m*	*Tb* 421_0 *s, n*
4201 *m*	*Tb* 420_0 *vs*
4193 *m*	*Tb* 419_0 *vs*
4184 *m*	*Tb* 418_0 *s*
4168 *m*	*Tb* 416_0 *vs, h*
4151 *m, h*	
4144 *m*	*Tb* 4145 *m*
4131 *m*	*Tb* 413_0 *vs*
4121 *d*	*Tb* 412_0 *vs*
4102 *d*	*Eu* 410_0 *d, h*
4029 *d, h*	
4022 *d, h*	*Eu* 4022 *vd, h*
3901 *d, h*	*Tb* 390_0 *vs, h*
3879 *d, h*	*Tb* 3880 *s, h*
3806 *m*	*Tb* 3805 *s, h*
3800 *m*	
3794 *m*	*Tb* 3795 to 378, *vs*, double
3781 *m*	
3575 *d*	
3372.7 *d*	
3165 *d*	*Gd* 3166 beginning of band
3158.2 *m*	*Gd* 3158.5 *s*
3155 *m*	*Gd* 3155.5 *m*
3152.7 *s*	*Gd* 3153.0 *s*
3146.2 *vs*	*Gd* 3147 *s, h*
3140.6 *s*	*Gd* 3140.5 *s*
3135.3 *s*	*Gd* 3134.0 *vs*
3129.4 *d*	*Gd* 3130 end of band
3122.3 *d*	
3120.2 *s*	*Gd* in CaF_2 3120 *vs*
3119.2 *s*	3118 *vs*
3114.9 *m*	3115 *vs*
3113.4 *d*	3113 *d*
3109.4 *d*	3110 *d*
3093.2 *m*	*Gd* 3094 *m, h*
3087.7 *m*	*Gd* 3088.5 *m, h*
2897.5	
2893	
2828.1 *d*	*Gd* 2828 *d*
2797.3 *vd*	
2790.7 *vd*	*Gd* 2789 *vd, h*
2786.3 *vd*	

Specimen 5. [Material kindly furnished by the late Dr. Charles Baskerville; occurring in colorless and in brownish specimens.] The fused specimens show only a few lines in the visible, most of which are due to samarium. There is also evidence of dysprosium and europium. Lines in the ultra-violet due to gadolinium are weak. Specimen shows bright green thermo-luminescence at comparatively low temperatures.

Discussion of Results

The presence of gadolinium is evident in all of the above specimens as well as in all the other fluorites of which the spectra were photographed in the ultra-violet. The other most prevalent and conspicuous rare earths identified are samarium, europium, terbium and dysprosium. Praseodymium appears to be present in some specimens. These results confirm the work of Urbain[1] who detected gadolinium in all the fluorites he examined. In chlorophane (not from the same locality as that examined by the author) he found samarium, erbium, terbium and dysprosium; in other specimens, terbium, praseodymium, samarium and dysprosium. This work is also in agreement with the results of Tanaka,[3] who, by an entirely different method, discovered the presence of samarium in samples of the same crystals as specimens 1 and 2 above.

It is of interest to note that the five most common rare earths which exist as impurities in fluorite have atomic weights which do not differ widely among themselves: Sm, 150.4; Eu, 152; Gd, 157.3; Tb, 159.2; Dy, 162.5. These elements all produce, in calcium oxide as diluent, lines which are narrower and sharper and more numerous than those which they produce in calcium fluorite. The extreme sharpness and relatively high intensity of some of the fluorescence bands in the fused fluorites at room temperature make further study of them a subject of considerable interest.

While the process of fusion and subsequent heating changes the bombarded part of the specimen from calcium fluoride to calcium oxide, both the original fluoride and the resulting oxide are crystalline in form. According to a suggestion made by Dr. E. C. Mendenhall, the sharpness of the lines in the luminescence spectra of substances containing minute quantities of rare earths may be explained if we assume that an atom of rare earth replaces an atom of the material used as diluent and forms an integral part of the regular crystal lattice of this material, for its position in the crystal structure would place upon its vibrations such limitations as to account for the sharpness of the lines in the spectrum of the light produced. This assumption may also explain why the luminescence spectrum of a given rare earth in one diluent, such as calcium fluoride, is radically different from that of the same earth in another diluent, such as calcium oxide,[7] for the limitations placed upon the vibrations by one crystal lattice are probably different from those imposed by another.

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[7] Urbain, Ann. de Chemie et de Phys. (8) **18,** 256 (1909)