

SOME PHYSICAL PROPERTIES OF NATURALLY IRRADIATED FLUORITE^{1,2}

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ABSTRACT

Five samples of purple fluorite found in association with radioactive materials, and a synthetic colorless control sample were studied and compared. Before and after heating, observations were made on specific gravity, index of refraction, unit-cell size, breadth of x -ray diffraction lines, and fluorescence. The purple samples became colorless on heating above 175° C. During the process, observations were made on color, thermoluminescence, and differential thermal analysis curves. There were strong correlations between the various physical properties, and it was found possible to arrange the samples in order of increasing difference in their physical properties from the control sample. This order apparently represents increasing structural damage by radiation; if so, it correlates with decreasing specific gravity, increasing index of refraction, broadening of x -ray lines, and increasingly strong exothermic reactions on annealing. The differences between the samples in index of refraction and x -ray pattern are largely eliminated on annealing. Annealing begins at 175° C.; thermoluminescence at lower temperatures is due to electrons escaping from the metastable potential traps, not the destruction of those traps which takes place on annealing.

INTRODUCTION

Purple fluorite is often found associated with deposits of radioactive material. Many workers have colored fluorite purple by exposing specimens to various sorts of ionizing radiation. It has also long been known that this purple color bleaches out on heating. The purple coloring has been ascribed to *F-centers*. These are regions of low potential energy in which electrons or ions are trapped in a metastable state, such that among the permitted increments of energy, there is a range corresponding to the absorption of visible light. Impurities may give rise to *F-centers* by providing permitted energy levels between those of the ordinary calcium fluoride structure, which normally has energy levels too far apart to permit electrons in the ordinarily filled orbitals to absorb visible light.

Omission of a fluoride ion would leave a gap surrounded tetrahedrally by positively charged calcium ions. Electrons may be trapped in the gap itself or in imperfections arising from the distortion caused by the gap. Or the gap may operate indirectly to trap electrons, as the various mechanisms that compensate for the charge of the missing ion—such as omission of cations or introduction of impurities of different charge—may themselves contribute to the formation of the “potential wells” in which electrons may be trapped.

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In short, any defects or imperfections in the structure that bring positive ions into a position such that electrons may be trapped between them may contribute to the purple coloring.

When irradiated fluorite is heated, the structure can readjust itself to the more stable state, eliminating defects, gaps, and areas of strain, and the coloration is destroyed.

DESCRIPTION OF THE SAMPLES

Five specimens of fluorite collected from radioactive deposits were chosen from the Harvard collection. Their descriptions follow.

Sample F1 from Wölsendorf, Bavaria. The fluorite is dark purple-black in color, the purple tint being apparent only by direct comparison with the jet-black uraninite on the same specimen. It is so nearly opaque that its optical properties were very difficult to determine. It has some very poorly formed cleavages, consisting largely of concave areas of minute surfaces reflecting light in approximately the same position. The fluorite is riddled with minute cracks. The specimen also has some patches of reddish-brown feldspar and cavities and fractures filled with secondary uranium minerals. The sample of fluorite for study was taken from within 6 mm. of the edge of the uraninite. The fluorite is very brittle, shattering to a powder very quickly and easily during the grinding process. When ground or broken with a hammer, the fluorite gives out a very sharp odor ascribed by Hoffman (1937) to HF and ozone, the result of free fluorine liberated by radioactivity. The material has been given the name antozonite, after the supposed evanescent gas, antozone. Earlier names were Stinkstein and Stinkfluss (Hausmann, 1847).

Sample F2 from Wilberforce, Ontario. The fluorite consists of a rodlike mass about 3 mm. across, completely buried in a crystal of uraninite. The material is so dark that the contact between the fluorite and the uraninite could not be seen, although irregular cleavages did develop in the fluorite mass, marking out its approximate extent. The material is so nearly opaque that the index of refraction could not be obtained. Locally, there was a dull, red-brown powder in and on the fluorite. The entire sample was crushed and separated by sink-float methods.

Sample F3 from the Clark fluorspar mine, Cardiff Township, Ontario. The fluorite is dull, dark purple, brittle and minutely cracked. It occurs as inclusions in and interstitial to aggregates of uranoan thorite. Apatite and diopside are also present in the specimen. On being crushed, it gives off an odor similar to that of sample F1. Grains of microscopic size were translucent. The average distance of the particles of the sample from the thorite was about 5 mm.

Sample F4 from Nippissing Syndicate, Harcourt, Cardiff Township, Ontario. It consists of translucent fluorite, colored a relatively light purple red. Flat cleavage planes several millimeters wide appear on the surface of the specimen. The fluorite is associated with calcite, apatite, sphene, diopside, and widely scattered uranoan thorite. It is transparent under the microscope and gives off no noticeable odor when ground. The fluorite is several centimeters away from the nearest uranoan thorite crystal.

Sample F5 is colorless synthetic fluorite made by the Harshaw Chemical Company. It consists of fused reconstituted material from southern Illinois. Many of the physical properties of this material were measured with great precision by R. D. Allen (1950), who reported this as sample 38.

Sample F6 from Wilberforce, Ontario. It consists of reddish calcite with irregular microscopic patches of virtually opaque fluorite. The calcite is in contact with uraninite. Within

4 mm. of the uraninite, the calcite-fluorite mixture is blue rather than reddish. The calcite consists of alternate light and dark layers about 1 mm. wide, the dark layers containing more fluorite. The fluorite was recovered by treating the material with acid. The grains are very rough and irregular in shape and tend to form loose aggregates that make the powder very difficult to handle. The material selected for the sample was about 15 mm. from the nearest visible uraninite.

Many of the physical properties of the samples before heating show strong correlations between themselves. It is possible to arrange the samples in order of decreasing difference of their properties, in general, from those of the control sample. To illustrate these correlations, the data will be listed in this order. Starting with the one most different in its properties from the control sample, the samples are F2, F6, F1, F3, F4, and F5.

SPECIFIC GRAVITY

Specific gravity was measured by preparing a mixture of methylene iodide and acetone in which the material was just suspended. The density of the liquid was then obtained by weighing it in a tared 25-ml. volumetric flask.

The purple fluorite samples all had a specific gravity considerably less than the control sample. The range for a single sample was narrow, on the order of 0.007 or 0.008 gm./cm.³. The values changed little with bleaching, indicating that the low specific gravity was due primarily to cracks rather than structural imperfections. According to Merwin (1911), the specific gravity of fluorite is 3.180 ± 0.001 .

TABLE 1. SPECIFIC GRAVITY OF FLUORITE SAMPLES

Sample No.	Before heating	After heating (1 hr, 600° C.)
F2	3.063 ± 0.004	
F6	porous	
F1	3.093	3.088
F3	3.105	
F4	3.142	3.139
F5	3.180	

X-RAY DIFFRACTION

The samples were run at 0.25° per minute on an x-ray diffractometer, using nickel-filtered copper radiation. On the high-angle lines, a scale factor of 4, a multiplier of 1.0, and a time constant of 2 seconds were used. The samples were packed by hand into the aluminum holders against a glass slide taped to the front. No binder was used. The x-ray unit was run at 40 kv, 20 ma.

Three values were determined for each $K\alpha_1$ line: the Bragg angle (2θ) of the intersection of the axis of symmetry for the upper part of the peak with the background level; the height of the peak above background, in arbitrary chart units; and, as a measure of line broadening, the distance between the axis of symmetry and the pen trace on the low-angle side, at half the height of the peak. The low-angle side of the peak was used to avoid the interference of the $K\alpha_2$ peak.

TABLE 2. CELL CONSTANT OF FLUORITE SAMPLES, a_0 IN Å AT 25° C.
($CuK\alpha_1=1.54050$ Å)

Sample No.	Unheated	Heated (1 hr, 600° C.)
F2	lines too broad	
F6	5.4633	5.4636
F1	5.4631	5.4635
F3	5.4635	5.4633
F4	5.4634	5.4632
F5	5.4633	

The values for the cell constant calculated from each line were plotted against the Nelson-Riley function and extrapolated to $\theta=90^\circ$ to give the final corrected a_0 value. The samples are virtually identical in cell size, and show no significant change with bleaching. The values in Table 2 can be summarized as $a_0=5.4633 \pm 0.0003$ Å at 25° C. Allen (1950) gives a value of 5.46295 ± 0.00010 Å at 20° C.

LINE BROADENING

The amount of structural imperfection is reflected in the width and height of the peaks. These values are also affected by the packing of the sample. Fortunately, the influence of the packing factor can be estimated.

TABLE 3. HEIGHTS OF PEAKS ABOVE BACKGROUND IN ARBITRARY CHART UNITS

Sample No.	(422) line		(531) line	
	Unheated	Heated (1 hr, 600° C.)	Unheated	Heated (1 hr, 600° C.)
F2	24		5	
F6	28	58	12	22
F1	29	46	11	15
F3	34	62	13	26
F4	51	58	19	30
F5	88		11	

If the differences are due entirely to the preparation of the sample, the width of the peak should vary as the height. If they vary inversely, as Tables 3 and 4 show, it can be assumed that the causes are of a structural nature. The (422) and (531) lines were selected for the tables because they are fairly intense high-angle lines. They represent spacings of 1.11 and 0.923 Å, respectively. For CuK α radiation, the values for 2θ are 87.3° and 113.0°.

TABLE 4. HALF WIDTH (LOW-ANGLE SIDE) AT HALF HEIGHT, IN HUNDRETHS OF A DEGREE 2θ

Sample No.	(422) line		(531) line	
	Unheated	Heated (1 hr, 600° C.)	Unheated	Heated (1 hr, 600° C.)
F2	19		50	
F6	17	6	27	10
F1	15	5	24	7
F3	7	5	17	8
F4	6	6	7	6
F5	4		7	

The increase in line broadening (Table 4) in the unheated samples from F5 to F2 evidently has a structural basis and represents increasing strain and imperfection in the crystal structure.

Regardless of the starting point, the samples after heating give results similar to those of the least imperfect natural sample, F4, before heating.

INDEX OF REFRACTION

A double-variation apparatus such as described by Emmons (1928, 1929) was used to measure the index of refraction. All measurements were made with the monochromator set on the value for the sodium *D* line ($\lambda=589 \text{ m}\mu$) as the temperature was varied from 25° to 40° C. Mixtures of amyl alcohol and mineral oil were used as the immersion media, the liquid being checked immediately in the Abbe refractometer that forms part of the equipment. Immersions of several dozen grains were prepared, and the stage was heated by circulating water until the immersion liquid reached and passed the range of index of refraction of the grains. The last indication of higher index and the first indication of lower index were noted; generally, the indices were about 0.0003 apart. Clearly, the sensitivity of the method is much greater than the accuracy, which is usually stated as ± 0.001 .

Allen's best values for the refractive index of fluorite (1950) were

obtained on sample F5 by the minimum deviation method. They averaged 1.43385 for sodium light at 20° C. This value was used in checking the calibration of the Abbe refractometer.

TABLE 5. INDICES OF REFRACTION OF FLUORITE SAMPLES
($\lambda=589 \text{ m}\mu.$) Temperature=25° to 40° C.)

Sample No.	Before heating	After heating (1 hr, 600° C.)
F2	Opaque	1.4348
F6	1.4363	1.4325
F1	1.4389	1.4348
F3	1.4381	1.4349
F4	1.4357	1.4354
F5	1.4338	

Once again, the heated samples, with the exception of the anomalous F6, are very similar and show approximately the same value as the unheated F4. Among the unheated samples, except for F6, the index decreases along with structural damage, as shown by x -ray line broadening, in the series F2 through F5.

As the specific gravity decreases, the index of refraction increases. This is completely contrary to expectation; normally, as fewer ions are available to be polarized by the electromagnetic fields of the light waves, the index should decrease. A convenient empirical measure of the degree of interaction between the light waves and the light-induced dipoles of the material is provided by the *specific refractive energy* of Gladstone and Dale (1864). It is equal to $(n-1)/d$, where n is the mean index of refraction and d is the density. This function varies in a more or less straight line when substances are combined in different proportions.

The specific refractive energy decreases markedly down the series to F5, as Table 6 shows. The possibility that the change is due to trace elements was tested by calculating a theoretical value from the results of the spectrographic analysis (Table 7). The quantities present were assumed to be the upper limit of the bracket in which the elements were reported. The results of this calculation are listed in Table 6.

TABLE 6. SPECIFIC REFRACTIVE ENERGIES OF FOUR FLUORITE SAMPLES

Sample No.	Observed	Calculated
F1	0.1419	0.136 (15)
F3	0.1411	0.136 (16)
F4	0.1387	0.136 (35)
F5	0.1364	

The specific refractive energies for the trace-element fluorides were calculated from data on crystalline fluorides or silicofluorides.

Allen (1950), in his study of ordinary stable fluorite, reached the conclusion that trace elements were of only limited importance among the factors causing anomalous indices of refraction. This is even more certainly true of these irradiated samples, although trace elements may play a role in determining the susceptibility of the fluorite to structural damage.

The rise in index of refraction is apparently caused by the ions in metastable positions. They interact more strongly with the passing light waves than similar ions in stable positions, hemmed in by high potential barriers. When the fluorite is annealed, the specific refractive energy decreases toward that of the control sample.

Structural damage by radiation is usually associated with lower, rather than higher, indices of refraction. In most of the samples studied, however, the ions have been very much heavier than in fluorite. As in fluorite, there is a marked decrease in density, which results in a lower index, but counteracting effects would be very much more difficult to observe.

TRACE ELEMENTS

Spectrographic analyses were obtained on purified material in order to determine the role played by trace elements in the coloring or structural distortion of the fluorite. Adequate material could be obtained only from samples F1, F3, and F4. F1, the most strongly affected sample, is the purest CaF₂ of the three, and F4, the least affected, contains the largest amount of trace elements, on the order of five to ten times as much as F1.

Except for the absolute amounts, the lists of trace elements are very similar in the three samples, and are essentially those normally found in fluorites: Sr, Fe, Al, Mg, and rare earths. The Cr may have been introduced by instruments used in the grain picking.

TABLE 7. SPECTROGRAPHIC ANALYSIS OF THREE FLUORITE SAMPLES

Per cent	F1	F3	F4
Over 10	Ca	Ca	Ca
0.1-0.5	—	—	Al Si Sr
0.05-0.1	—	Sr Fe Y	Fe
0.01-0.05	Al Si Fe Sr	Si Al Mg	Y Mg
0.005-0.01	Y	—	—
0.001-0.005	Ba Cr	Cr Pb Yb	Cr
0.0005-0.001	Ti	Ba	Ba
0.0001-0.0005	Mg Yb	Ti	Ti Yb

Table 7 gives the spectrographic results as determined by K. E. Valentine of the U. S. Geological Survey. Fluorine was known to be present, and therefore was not determined. This determination requires a special process.

BEHAVIOR ON HEATING

When heated the samples pass through various shades of reddish purple and lavender until they become nearly colorless. By far the greater part of the bleaching, at temperatures over 300° C., is accomplished in the first few minutes. The rate of the process continuously decreases, and complete bleaching takes much longer. At 500°, the samples are completely bleached in an hour. At 470°, the samples are still light lavender at the end of 6 hours. Seventy hours is sufficient to bleach the samples completely at 400° C. but 18 hours at 370° was not. Sample F1 was completely bleached at 230° in 6 days. After 10 days at 185°, it became lighter in color and showed narrower x -ray lines. After the first few minutes the different samples being treated at the same temperature had virtually the same color, and thereafter they reacted the same way to further heating.

The increase in sharpness of x -ray line with progressive heating of sample F1 is shown in Table 8.

TABLE 8. HEIGHT AND BREADTH OF (422) AND (531) LINES AT DIFFERENT STAGES OF BLEACHING OF SAMPLE F1

Time	Temp.° C.	Color	Breadth at $\frac{1}{2}$ height		Height	
			(422)	(531)	(422)	(531)
Unheated		Purple-black	15	24	29	11
9 days	186	Purple	11	11	37	11
9 days plus	186	Light violet	9	14	39	14
6 days	202					
6 days	230	Colorless	8	12	45	14
1 hr	600	Colorless	5	7	46	15

DIFFERENTIAL THERMAL ANALYSIS

The samples were run on the differential thermal analyzer at Massachusetts Institute of Technology by Danforth Kelley. The equipment and methods have been described by Whitehead and Breger (1950). The samples were run in air, with the control sample, F5, in the other thermocouple well. Unfortunately some of the samples could not be

purified completely before heating, and, when they were rendered colorless, patches of reddish material became visible in cracks and on the surface. This introduced an extraneous peak that interfered with the peak caused by the bleaching. Nevertheless, the two peaks could be separated graphically, if it is assumed that they are symmetrical.

All the patterns showed an exothermic peak at 360° C. when the temperature was increased at the rate of 20° per minute, and at 320° when the temperature rose 10° per minute. This peak plainly does not represent any critical point or stage in the reaction. The reaction rate increases as the temperature is raised and decreases as the reaction approaches completion. The peak represents the maximum rate. The pen trace begins to depart perceptibly from the center line at approximately 175° C. in all the runs. The height of the 360° peak in millimeters is given below, after graphical correction for the interfering peak in F3. Note that this is the same order as is shown by the tables of decreasing *x*-ray line broadening (Tables 3 and 4), and increasing index of refraction (Table 5).

TABLE 9. HEIGHT OF PEAKS AT 360° C. IN DIFFERENTIAL THERMAL ANALYSIS PATTERNS, RUN AT 20° PER MINUTE AGAINST SAMPLE F5

Sample No.	Height (in mm.)
F2	55
F6	16
F1	15
F3	12
F4	7

Under comparable conditions, the low-quartz high-quartz inversion gives a peak 46 mm. high at 573° C.

THERMOLUMINESCENCE

A borosilicate glass front for a muffle furnace was improvised from a beaker, so that the thermoluminescence of the fluorite samples could be observed in a darkened room. At 300° C., each individual grain flared up suddenly as it reached the threshold temperature for thermoluminescence. It would start glowing brightly, standing out clearly from the other grains already glowing. Within about 30 seconds, it would fade into the general glow which continued to dim as the material bleached. Raising the temperature would not revive the thermoluminescence to any great extent; in fact, it accelerated the decline.

The samples were observed from time to time by the usual room illumination. These subjective observations strongly suggest that the

intensity of thermoluminescence is proportional to the rate of bleaching. This visible light represents a very small part of the energy released in going from the metastable purple state to the stable colorless state. It is probably caused by the fall-in of the entrapped electrons. By far the greater changes are associated with the destruction of the structural traps themselves.

The process is of course irreversible. No such effects are observed on heating already bleached fluorite.

The temperature at which thermoluminescence began could be determined fairly precisely. In the course of heating in a crucible on a hot-plate, the entire sample was glowing 15 seconds after the first trace of thermoluminescence. The temperature was determined from a suspended mercury thermometer, the bulb of which was not in contact with the sides of the crucible.

As the temperature increased, thermoluminescence continued. When the temperature was permitted to drop, the luminescence ceased at a somewhat higher temperature than that at which it had started. When the temperature was again increased, luminescence started at the temperature at which it had been quenched. This cycle could be repeated many times, with a higher quenching temperature at each time. At the end of 15 minutes of luminescence, in which the temperature had gone to 145° C., the quenching temperature for sample F1 had risen from 65° to 130°. This behavior suggests the progressive emptying of more and more stable electron traps as thermoluminescence proceeds. If a sample is held at a stable temperature in this range, the luminescence declines asymptotically. The color is not noticeably affected until a temperature of about 175° is reached.

This evidence seems to indicate that thermoluminescence is caused by a mechanism that is distinct from that causing *x*-ray line sharpening, change of index of refraction, and the other effects related to the destruction of the purple color. The thermoluminescence is apparently caused by the infall of electrons, which begins at a temperature of about 65° C. The other changes involve destruction of the structural traps containing the electrons.

The temperatures at which thermoluminescence began are as follows:

TABLE 10. TEMPERATURE (°C.) OF BEGINNING OF THERMOLUMINESCENCE

Sample No.	Temperature (°C.)	Sample No.	Temperature (°C.)
F2	58	F3	78
F6	66	F4	65
F1	64	F5	—

These results are in essential agreement with those of Daniels and Saunders (1951), who studied thermoluminescence artificially induced in fluorite by means of cobalt 60. Using their combination furnace and photometer, they found that fluorites of various colors gave two groups of coalescing peaks: one set from 50 to 150° C., and the other set starting at 175° C. and continuing to red heat. In certain samples, only one of the sets was obtained.

None of the samples in this study fluoresced in long or short wavelength ultraviolet radiation, either before or after bleaching. All samples fluoresced blue in x -rays. Generally the x -ray fluorescence was stronger after bleaching as the sample did not absorb so much of the visible light it produced.

RE-IRRADIATION

The samples were partly recolored by exposure to unfiltered copper-target x -rays for 48 hours. The purple color produced was much deeper in some samples than in others. Sample F6 developed a light-purple streak in the center of the x -ray spectrometer sample mounting, in the course of a 20-minute spectrometer run. Sample F1 showed a barely perceptible darkening after being taped to the x -ray tube window for 48 hours.

The color was not stable. Forty-eight hours after the end of irradiation, all the samples had faded considerably. After a week in the dark at room temperature, the color was virtually gone.

Several of the samples were taped to the surface of a short-wavelength 15-w Sylvania mercury-vapor lamp. After 17 hours of exposure to ultraviolet radiation, no change was noted in the samples.

A cleavage fragment of yellow fluorite from southern Illinois was exposed to x -rays for 48 hours, then etched for 1 minute with 1:1 sulfuric acid. The etching of the purple irradiated spot was compared to that of the unexposed fluorite under the binocular microscope. No difference was observed.

Przibram (1954) describes the coloring of fluorite by alpha radiation from radium. It was possible to establish an apparently stable absorption band in the middle of the spectrum by months of exposure. Nevertheless, a certain amount of recovery took place at the red end of the spectrum; the absorption decreased gradually to the pre-irradiation level. The peak of the absorption band gradually shifts from the red end to the center of the visible spectrum as exposure continues. As it does so, it becomes less subject to this recovery effect.

Allen (1950) measured the index of refraction of fluorite prisms before and after irradiating the edge with x -rays for 24 hours. Although striking

changes of color were readily obtained, there was no observable change in the index of refraction.

CONCLUSIONS

On being exposed to radioactivity, fluorite undergoes a number of changes in its physical properties. The fluorite turns purple. The index of refraction increases. Cracks develop and the apparent specific gravity decreases. The x -ray diffraction lines broaden and decrease in height. All of these effects, except the specific gravity change, can be reversed in an exothermic reaction that takes place at a perceptible rate above 175° C. These phenomena have a structural origin; they are apparently caused by nuclear particles disrupting the structure along their paths, after which the material recrystallized imperfectly. Raising the temperature permits the sample to recrystallize again with fewer strains and imperfections. Specimens of irradiated fluorite can be placed in a definite order of intensity of structural damage and strain, and their properties, as well as the energy released in recrystallization, vary according to this order.

The intensity of structural damage cannot be used as a method of age determination, as Hurley and Fairbairn (1953) have done with zircon. Even if it were possible to make an adequate estimate of the amount of external radioactivity, the method could show only the time since the sample cooled below 175° C. At higher temperatures, the damage was healed as quickly as it occurred.

Nor can the purple coloring be used as a geologic thermometer. It indicates that the fluorite was exposed to ionizing radiation for some time at temperatures below 175° C. But most specimens reach the observer in this condition at ordinary surface temperatures and with the radioactive material still associated with the fluorite. No geologic thermometer is needed to deduce this information.

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