

Article

Comparative Study on Gemological and Mineralogical Characteristics and Coloration Mechanism of Four Color Types of Fluorite

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Abstract: Fluorite has been attracting the attention of gemstone mineralogists because of its rich color and excellent fluorescence properties. This paper studied fluorite with three color types (blue, green, and white) and five blue-purple fluorites with an alexandrite effect. Through the study of their structure, composition, and spectral characteristics, the gemological and mineralogical characteristics and coloration mechanisms of different color types of fluorites are compared and analyzed. The results show that the color of fluorite is caused by multiple color centers. Blue fluorite is associated with $Y^{3+}-F^{-}$ color center, while green fluorite is associated with a $Y^{3+}-Ce^{2+}-F^{-}$ color center and Sm^{2+} color center, and white fluorite contains vacancy color center. The color of white fluorite is a mixture of yellow tones produced in visible light and blue fluorescence under UV light. Blue-purple color is caused by the colloid calcium color center and $2F^{-}$ color center, and its changing from blue-purple to red-purplish (alexandrite effect) are due to colloidal calcium nanoparticles caused by radioactive element Th.

Keywords: fluorite; gemological characteristics; mineralogical characteristics; alexandrite effect; coloration mechanism



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1. Introduction

Fluorite is a very important gemstone and mineral resource which plays a pivotal role in optics, metallurgy, electronics, and other fields [1–4]. Fluorite is also a natural ornamental stone because of its extremely beautiful appearance [5]. Fluorite is one of the few gemstones that are very active in response to light, and the colors of natural fluorite almost cover all the colors in nature [6]. In a few fluorite varieties, the color changes when observed in sunlight or artificial incandescent light (e.g., alexandrite effect) [7,8]. Most fluorite varieties have fluorescence, and some of them have phosphorescence and thermoluminescence properties [9–12].

At present, the chromogenic mechanism, fluorescence mechanism, and alexandrite effect of fluorite have been the focus of scholars' research. The major component of fluorite is CaF_2 , and pure fluorite is colorless [13]. The chromaticity mechanism of fluorite can be divided into three categories: chromaticity caused by impurities such as rare earth elements and transition metals mixed in the lattice [14–16], vacancy color center caused by crystal defects [17–21], organic matter chromatism, that is, secondary organic matter in fluorite crystals (such as fluid-inclusions or carbon nanoparticles) leads to chromatism of fluorite [10], which is a kind of allochromatic color. The emission characteristics of fluorite fluorescence depend on the environment of mineral growth and the impurities it contains [22]. Natural fluorite contains rare earth elements (such as Eu, Pr, Dy, Ho, etc.) inside, which cause electron leaps resulting in fluorescence after being excited by UV

light [23–28]. Some fluorite species have thermoluminescence effects resulting from a large number of defects in the crystal lattice [29,30]. Although some authors [24,25] suggested that the alexandrite effect of fluorite is related to the colloidal calcium color center or $2F^-$, such a hypothesis has not yet been verified [31].

At present, there are few comprehensive comparative studies on different color fluorite and color-changing fluorite, and there is still a lack of research on fluorite with the alexandrite effect. In the existing reports, the reasons for the alexandrite effect of fluorite have not been deeply studied. Based on this, this paper considers a set of natural fluorite crystals with three different colors and five fluorites with color changes in different light conditions (e.g., alexandrite effect) to assess the coloration, color-changing, and fluorescence mechanisms. This work will deepen the understanding of the thermal response of fluorite under fluorescence and enhance the understanding of the fluorite color change effect, laying the foundation for the application of fluorite in the photothermal change environment.

2. Materials and Methods

2.1. Fluorite Samples

The samples for the experiment (Figure 1) were two blue fluorites (B-1, B-2) and three green fluorites (G-1, G-2, G-3) from Jinhua, Zhejiang Province, China, two white fluorites (W-1, W-2) from Shangbao, Hunan Province, China, and five fluorites with color change effect from Benxi, Liaoning Province, China (deep blue-purple fluorite is numbered DBP-1, DBP-2 and light blue-purple fluorite are numbered LBP-1, LBP-2, LBP-3). Blue fluorite and green fluorite have a better octahedral crystal form, color-changing fluorite has a clustered crystal structure, and white fluorite has an irregular crystal form.



Figure 1. Appearance of fluorite samples for experiment.

2.2. Methods

Conventional gemological characterization testing instruments include color refractometers, gemological microscopes, electronic balances, dichroscopes, polariscopes, spectroscopes, and UV fluorescent lamps.

Structure and composition characteristics include X-ray powder diffraction, X-ray fluorescence spectrometer, electron probe micro-analysis, Raman spectra test, and infrared absorption test. The instrument used for X-ray powder diffraction is Dmax12KW, with CuK α rays and a scanning speed of 0.17°/s. The composition of fluorite was tested using the EDX-7000 Energy dispersive X-ray fluorescence spectrometer produced in Tsushima, Japan, with detection limits of 0.1% and the EPMA-1720 EPMA, manufactured by Shimadzu, Japan, with detection limits of 500 ppm. The voltage was 15 KV, and carbon injection was done before the test. The HR-Evolution microscopic Raman spectrometer produced by HORIBA in Japan was used for the Raman spectroscopy test. The experimental voltage was 220 V, the current was 10 A, and the laser was 532 nm. The infrared spectroscopy was collected by a TENSOR 27 Fourier infrared spectrometer from Germany using the KBr compression transmission method.

Spectroscopic characterization tests include the photoluminescence emission (PL) spectrum test and the UV-Vis absorption spectrum test. The photoluminescence emission (PL) spectra were tested by Hitachi F-4700 fluorescence spectrometer with a scanning rate of 240 nm/min and detection voltage of 500 V. UV-Vis absorption spectrum was tested using UV-3600 UV-VIS spectrophotometer produced by Shimadzu, Japan. Polishing was finished before the test. The measuring range was 0.5 nm, and the reflection method was used for the test.

The following flow chart (Figure 2) shows the various tests performed and the results obtained.

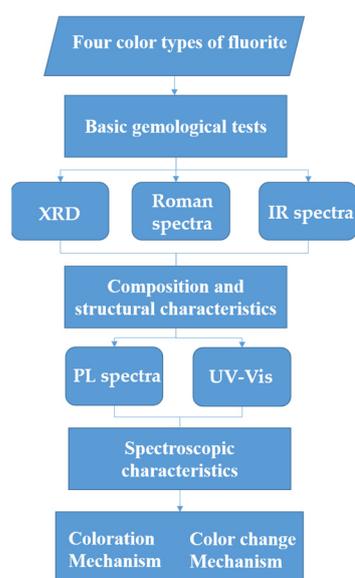


Figure 2. Experiment flow chart.

3. Results and Discussion

3.1. Basic Gemological Features

The refractive index and relative density of the samples (shown in Table S1 for specific data, see Supplementary Materials) are comparable to those of natural fluorite in previous studies [8]. Fluorite of blue, green, and white colors emits strong blue-white fluorescence when excited by a long-wave UV lamp, and weak purple fluorescence under a short-wave UV lamp. However, the fluorescence intensity of fluorite with a color change effect is weak, and all the samples have no phosphorescence. DBP-1 appears blue-purple in daylight and purplish-red in incandescent light (Figure 3).

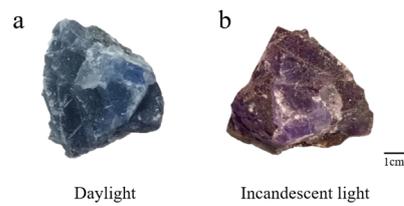


Figure 3. Photographs of color-changing fluorite DBP-1 (a) in daylight; (b) in incandescent light.

There are a large number of stepped fractures on the surface of fluorite (Figure 4b), and the internal ridges can be seen in fluorite (Figure 4a,c). Growth mounds (Figure 4d) and poly patterns (Figure 4e) were observed on the surface of the color-changing fluorite, and white bands (Figure 4f) were observed inside.

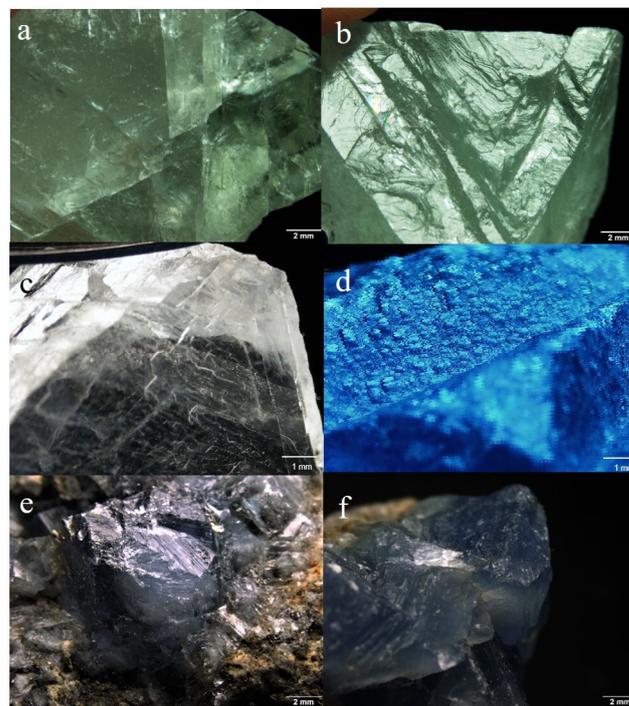


Figure 4. Characteristics of fluorite samples under the gemological microscope: (a) cleavage lines; (b) stepped fracture; (c) internal cleavage plane; (d) growth mound; (e) coniferous lines; (f) internal bands.

3.2. Structure and Composition Characteristics

To explore the microscopic phase composition of fluorite with different colors, the Raman spectra of four fluorites were collected. It can be seen from Figure 5a that the Raman shift of the samples is located in the range of $100\sim 1000\text{ cm}^{-1}$, and the characteristic absorption peak of fluorite appears around 320 cm^{-1} . The white fluorite only has a Raman peak at 320 cm^{-1} , while the non-white fluorite also has peaks at other locations. The Raman peak positions for the non-white samples are generally consistent, but the relative intensity is different. The Raman peaks at $195, 251, 271,$ and 438 cm^{-1} are related to irradiation, while the peaks at $505, 560, 606, 621,$ and 645 cm^{-1} are related to a small number of rare earth elements in fluorite [24]. The Raman spectrum for barite inclusion of light blue-purple fluorite was discovered (Figure 5b), and barite may be the primary mineral in the interior band of the color-changing fluorite. (Figure 4f).

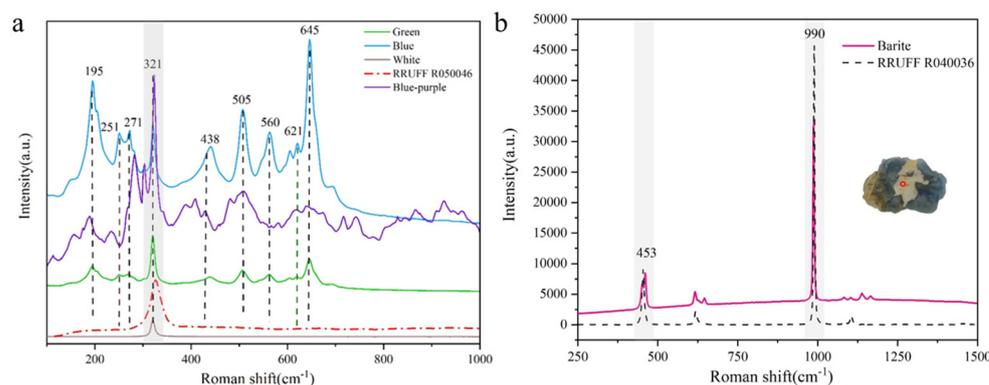


Figure 5. (a) Raman spectra of all color fluorite samples; (b) Raman spectra of barite in light blue-purple samples.

To explore the composition differences of fluorites with different colors, we carried out X-ray fluorescence spectroscopy and electron probe micro-analysis Data tests (shown in Tables S2 and S3 for results). The main elements of the four samples are Ca and F. In addition, there are also metal elements (Na, Mg, Zn, K, Sr, Rb, Y), transition metal elements (Fe, Co, Ni, Cu, Zr, Mn), non-metallic elements (Si, Br, S, elements in inclusions), radioactive elements (Th). The average Ca contents of blue, green, white, light blue-purple and dark blue-purple fluorite are 50.21%, 50.47%, 50.931%, 50.801%, and 50.492%, respectively. The average F contents are 48.89%, 48.102%, 48.505%, 48.985%, and 49.088%, respectively. The content of Ca in white and blue-purple fluorite is the highest, while the content of Ca in blue fluorite is the lowest. Except for the white fluorite sample, Y element was detected in other fluorite samples, indicating that Y had a great influence on the coloration of fluorite [17]. This exists in color-changing fluorite.

In fluorite, there are five different types of infrared absorption peaks (Figure 6a). The first is the characteristic peak of fluorite, which is usually located in $1060\sim 1080\text{ cm}^{-1}$; the second type, the characteristic absorption peak of CO_3^{2-} ion, is located at $1530\sim 1320\text{ cm}^{-1}$; the third type, O-H bending vibration, is located at about 1640 cm^{-1} ; the vibration of organic groups, at a distance of approximately 2928 cm^{-1} , is the fourth; the fifth type, O-H stretching vibration, is located at $3700\sim 3200\text{ cm}^{-1}$. Among them, the vibration of O-H indicates that there may be structural water in fluorite [32]. G-1 shows a super-strong hydroxyl peak, which is due to the fact that the test is done on a rainy day and there is a large number of water molecules in the air. The presence of CO_3^{2-} in fluorite may be related to calcite inclusions. In addition, there are infrared absorption peaks of $2360\sim 2364\text{ cm}^{-1}$ in fluorite samples, which may be caused by asymmetric stretching vibration of CO_2 in the air [33].

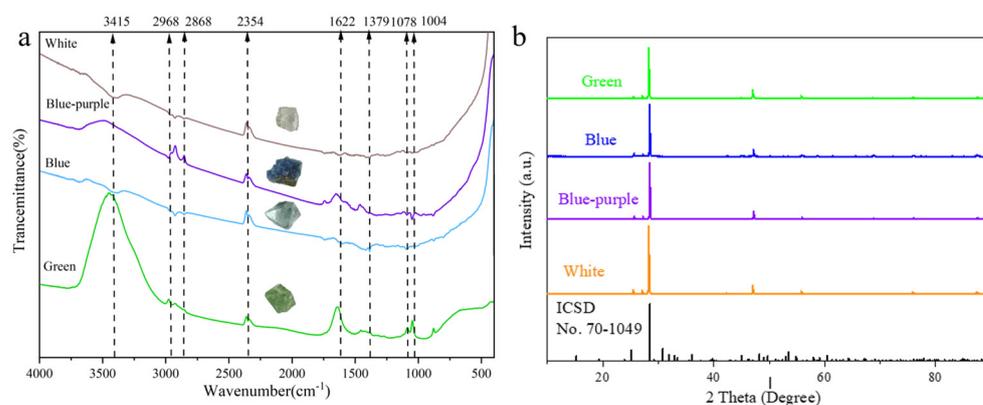


Figure 6. (a) IR spectra; (b) X-ray diffraction patterns of four color types of fluorite.

The X-ray diffraction spectra of the four color types of fluorite match the standard card for fluorite (ICSD No. 70-1069) (Figure 6b). The diffraction peaks of the samples appeared at 2-Theta of 28.339°, 47.124°, 55.905°, 76.056°, and 87.637°, and the diffraction intensity was the strongest at 28.339°, same as the previous research results [24]. All fluorite diffraction peak positions have a small range of offsets and small angle peaks, which may be related to the substitution of impurity elements for Ca. The calculated cell parameters (Table 1) differ from the standard card. There are K and Sr metal elements in the white fluorite, and the radii of K and Sr are larger than Ca, resulting in larger unit cell parameters. The types of elements in blue, blue-purple, and green fluorite are more complex. The combined action of these elements leads to the deviation of unit cell parameters, and the minimum relative density of fluorite with color change effect may be due to the presence of radioactive element Th.

Table 1. Crystal cell parameters of four color fluorite and standard card.

Sample Number	a, b, c (Å)	Cell Volume (Å ³)	Fit (R)	Relative Density (d)
White	5.4595	162.72	8.35%	3.19
Green	5.4358	160.61	7.33%	3.23
Blue	5.4320	160.28	7.29%	3.24
Blue-purple	5.4629	163.03	11%	3.18
ICSD No.70-1049	5.4502	161.90		3.20

3.3. Spectroscopic Characterization Tests

3.3.1. Luminescence Properties

We studied the photoluminescence emission (PL) spectra of fluorite at the excitation wavelengths of 365 and 254 nm to investigate the cause of the variation in PL emission (Figure 7a,b). The PL emission spectra of blue, green, and white fluorites are basically similar, and the emission peaks are 398 and 410 nm under the excitation of 365 nm. Under the excitation of 254 nm, the PL emission peak is at 468 nm, while the PL emission peak of color-changing fluorite under a long wave is mainly at 410 nm, and the intensity is weak.

The presence of rare earth elements and Y is the reason why fluorite fluoresces [23–28]. The emission peaks at 398 and 410 nm are caused by the $4f^6_5d \rightarrow 8s_{7/2}$ transition of Eu^{2+} [25]. There are two explanations for the emission peak at 468 nm, one is that it is caused by the $2D_{3/2} \rightarrow 2F_{7/2}$ of Ce^{3+} [34]; one is believed to be caused by $3H_4 \rightarrow 3P_1$ of Pr^{3+} [24]. In this experiment, a narrow band peak is observed, but the emission peak of Ce^{3+} is a broad band, while the emission peak of Tm^{3+} is located at about 471.1 nm, which is closer to the original peak. Therefore, the emission peak at 468 nm is related to the strong electron transition of Tm^{3+} [25]. The emission center at 452 nm is caused by $1D_2 \rightarrow 3H_4$ of Tm^{3+} [26]. Pr^{3+} ($3H_4 \rightarrow 3P_0$) is the source of the emission peak at 482–483 nm, and Tb^{3+} ($5D_4 \rightarrow 3F_6$) is the reason for the emission peak at 493–494 nm. Er^{3+} is the cause of the emission peak at 540 nm ($4S_{3/2} \rightarrow 4I_{15/2}$) [27,28]. The fluorescent properties of the four types of fluorite samples are shown in Table 2.

For the sake of exploring the change of fluorite fluorescence with different temperatures, the white fluorite sample, and color-changing fluorite sample were excited by 365 nm ultraviolet fluorescence, and their PL emission spectra at various temperatures were evaluated. The outcomes are depicted in Figure 7c,d. In Figure 7c, the main emission peaks of white fluorite at 398 and 410 nm at 25 °C show a blue shift and red shift respectively, when heated, and the fluorescence intensity generally weakens when temperature changes, showing a downward-upward-downward trend. Some studies have shown that the intensity of the main emission peaks of colored fluorite shows an upward-downward trend during heating, and the overall position of the emission peaks presents a redshift [24]. This experiment showed a more complex change trend, which may be due to different rare earth elements contained in different fluorite samples. The different positions of the main emission peaks of fluorite at different temperatures may be due to the differences in the radioactive elements that cause fluorite to emit fluorescence at different temperatures [35].

The maximum emission wavelength of the color-changing fluorite is maintained at 406 nm when the temperature is raised, and the fluorescence intensity is generally increased, which may be caused by the presence of lattice defects [30], and the major causes of these defects are the replacement of impurities and radioactive irradiation.

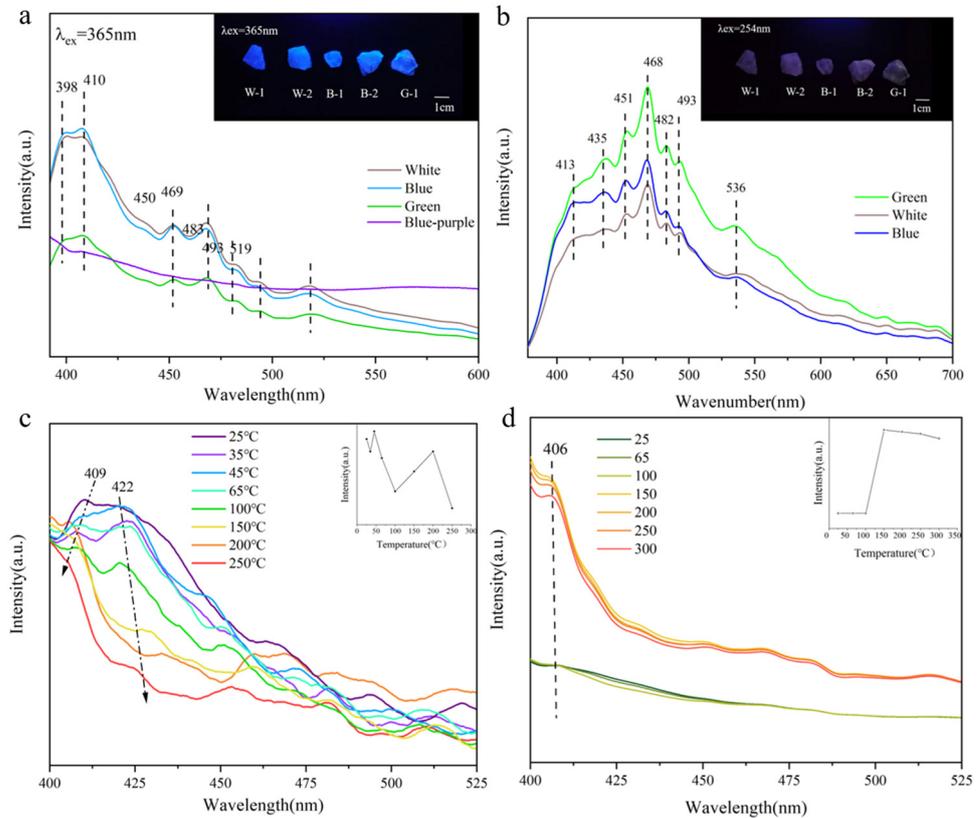


Figure 7. (a) Emission spectrum of samples at 365 nm; (b) Emission spectrum of samples at 254 nm; (c) Emission spectrum of white fluorite at an excitation wavelength of 365 nm at 25 °C–250 °C; (d) Emission spectrum of color-changing fluorite at an excitation wavelength of 365 nm at 25 °C–300 °C.

Table 2. The fluorescent properties of the four types of fluorite samples.

Color	Emission Lines	Possible Rare Earth Ions	Electronic Transitions
Blue	398 and 410 nm	Eu ²⁺	$4f^6_5d \rightarrow 8S_{7/2}$
	468 nm	Tm ³⁺	$1G_4 \rightarrow 3H_6$
	452 nm	Tm ³⁺	$1D_2 \rightarrow 3H_4$
Green	482–483 nm	Pr ³⁺	$3H_4 \rightarrow 3P_0$
White	493–494 nm	Tb ³⁺	$5D_4 \rightarrow 3F_6$
Blue-Purple	540 nm	Er ³⁺	$4S_{3/2} \rightarrow 4I_{15/2}$
	398 and 410 nm	Eu ²⁺	$4f^6_5d \rightarrow 8S_{7/2}$

3.3.2. UV-Vis Spectra

To obtain the coloration mechanism of fluorite with different colors, we tested the ultraviolet-visible absorption spectra (Figure 8a). We used the reflection method to test, so the absorption was located at the wave trough. Table 3 shows the color centers corresponding to different fluorite colors and their absorption peaks in the existing literature.

Table 3. Characteristic absorption peak and peak assignment of fluorite in UV-Vis spectrum (unit: nm).

Color	Possible Causes	Absorption		References
		Main	Secondary	
Blue	Y ³⁺ -F ⁻ Center.	300~400	500~600	[14,15]
	Colloidal calcium	580	/	[14,17,19]
	2F ⁻ center	580	/	[36]
Green	Colloidal calcium	573~600	/	[14,17,19]
	Sm ²⁺	440	611	[14,16]
Purple	Y ³⁺ -Ce ²⁺ -F ⁻	300	590 and 712	[14,16]
	Colloidal calcium	570	/	[14,16,17,19]

The coloration of blue fluorite is related to the absorption peaks at 423, 449, and 610 nm. 418 and 319 nm are related to the Y³⁺ color center [14], and 610 nm is related to Y³⁺-F⁻ color center or colloidal calcium color center. The combined color center of Y³⁺-F⁻ is a type of REF color center. Figure 7b shows the model of the REF color center, which is composed of an F vacancy, a trivalent rare earth ion, and two electrons revolving around them, such as the Y³⁺-F⁻ color center [15]. Based on the composition test, there is a Y element in blue fluorite, which is strong evidence that it is colored by Y³⁺-F⁻ center. The colloidal calcium color center is produced by the irradiation of fluorite, and the maximum absorption band is 580~650 nm. According to the size of colloidal particles, the maximum absorption generated is transferred from the red area to the yellow area, making the color of fluorite change from green to blue and then to purple [17]. The blue colloidal calcium color center corresponds to a broad peak of about 580 nm [19], while the absorption peak of the blue fluorite sample reaches the strongest at about 360 nm, which indicates that blue fluorite is not colored by the colloidal calcium color center.

The coloration of blue-purple fluorite is related to the absorption at 423 and 580 nm. The absorption peak at 580 nm may be caused by the colloidal calcium color center and 2F⁻ center. The presence of radioactive elements such as U, Th, and others causes the color center of colloidal calcium. After irradiation, Ca will gather to produce calcium colloid [14], and the remaining F will produce an F⁻ color center. The blue-purple fluorite contains the radioactive element Th. Studies have shown that the rare earth content of natural blue fluorite caused by colloidal calcium is very low [16]. The fluorescence intensity of blue-purple fluorite is very low at room temperature, which confirms the existence of a colloidal calcium color center laterally. The cause of light blue purple is that the fluorite sample is mixed with other minerals (barite), resulting in a white hue.

The main absorption peaks of green fluorite are at 450 and 426 nm, and the secondary absorption peaks are at 586 and 713 nm. These absorption peaks are probably related to Y³⁺-Ce²⁺-F⁻ color center and Sm²⁺ color center. The Y³⁺-Ce²⁺-F⁻ color center absorption band is located at 230, 335, 400, 590, and 712 nm. 590 nm and 712 nm correspond to the ¹A₁→¹E transition of Y³⁺-Ce²⁺-F⁻ color center, and the sharp band at 306 nm corresponds to the 4f-5d transition of Ce³⁺. 425 and 449 nm are due to Sm²⁺ color centers, which are related to the 4f⁶→4f⁵5d¹ transition. The maximum absorption peak of the colloidal calcium color center is about 575~650 nm, while the maximum absorption peak of the green fluorite sample is about 442 nm. The absorption peak of the long wave of green fluorite is double peak absorption, not single peak absorption of colloidal calcium color center.

It is worth noting that white fluorite has absorption at 212, 248, 312, and 362 nm, different from the non-absorption in the previous research [37]. The absorption at 212 and 312 nm is related to the vacancy color center on the Ca²⁺ vacancy [20]. The absorption peak at 362 nm is related to the holes in the center of the eight F⁻ sublattices (Figure 8c), which is produced by the incorporation of alkali metals such as Na and K [21]. Alkali metal element K is detected in white fluorite, which proves this view. The 365 nm purple absorption band can produce yellowish body color, but it appears white. This is because white fluorite mixes strong blue-white fluorescence with yellowish body color, making itself whiter in sunlight.

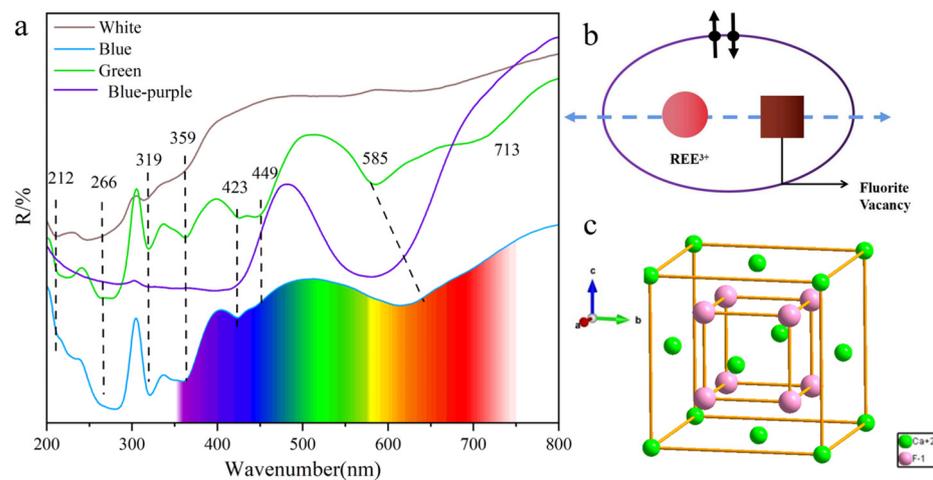


Figure 8. (a) UV-Vis spectra of fluorite of four colors; (b) REF color center model; (c) vacancy color center model. * b, c are adapted with permission from Ref. [15]. 1971 Staebler and Ref. [20]. 1963 O'Connor.

The large absorption band centered at 412 nm and 577 nm in fluorite with color changing effect, is shown in Figure 9. The light transmission zones A and B are located on each side of the absorption band with its center at 577 nm. Distinct hues under varying light sources are produced by the two light sources' different transmission ratios in light transmission zones A and B. The absorption at 577 nm is caused by the colloidal calcium color center or $2F^-$. The irradiation of the fluorite lattice or the doping of transition metal and rare earth elements is associated with the creation of the $2F^-$ color center [24,25]. There are transition metal elements Fe, Zn, Mg, Cr, Ti, Na, Cu, K, Mn, and rare earth elements Y in the color-changing fluorite, which are easily substituted with Ca^{2+} in the same phase. However, it's important to note that the color-changing fluorite has fewer rare earth and transition metal elements on average (0.3305%) than other fluorites (0.964%). Therefore, the color change effect of blue-purple fluorite is probably caused by the aggregation of Ca in the form of colloid caused by the radioactive element Th.

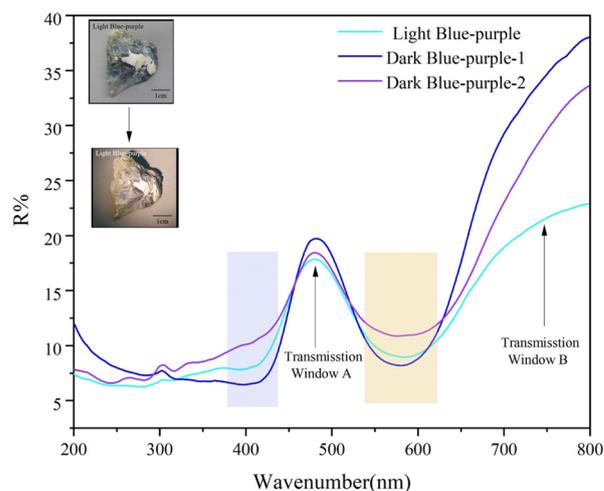


Figure 9. UV-Vis spectrum of color-changing fluorite.

4. Conclusions

Ca and F make up the majority of the components in the four different color kinds of fluorite samples, along with radioactive elements, rare earth elements, transition metal elements, and non-metallic elements (elements in inclusions). The color of fluorite is

different because of its color center combination. Blue fluorite is associated with $Y^{3+}-F^{-}$ color center, green fluorite is associated with the $Y^{3+}-Ce^{2+}-F^{-}$ color center and Sm^{2+} color center, and white fluorite contains a vacancy color center, whose color mixes yellow tone produced by the color center and strong blue fluorescence into its white body color. Blue-purple fluorite's coloring is brought on by colloid calcium and the $2F^{-}$ color center. The presence of the radioactive element Th also contributes to the color-changing effect by causing the aggregation of Ca into the colloid. These results are helpful to deepen the understanding of the coloration of fluorite and broaden the application of fluorite as fluorescent material in a high-temperature environment. The chromogenic mechanism of color-changing fluorite will be further studied in the future. The direct evidence for the presence of chromogenic and rare earth ions needs to be proven by subsequent studies.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst13010075/s1>, Supporting document Table S1. Basic gemological properties of fluorite samples; Supporting document Table S2. X-ray fluorescence spectral analysis data of fluorite of four colors; Supporting document Table S3. Electron Probe Data of fluorite in blue, blue-purple, green and white.

Author Contributions: Y.L., doing experiments and writing the original manuscript; Q.G., reviewing and editing; L.L. (Liangyu Liu), making analysis; S.Z., translating; Q.L., translating; L.L. (Libing Liao), review and editing. All authors have read and agreed to the published version of the manuscript.

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