

Article

Color Depth Gradient in Color-Change Fluorite from Brazil: A Multi-Spectroscopic Study on the Coloration Mechanism

Nan Jiang ¹, Geng Li ^{1,*} and Fabian Dietmar Schmitz ²

¹ School of Gemmology, China University of Geosciences (Beijing), Beijing 100083, China; 2009240035@email.cugb.edu.cn

² Rhein Main Gem Consulting, Forsterstraße 4, 55118 Mainz, Germany; fabian.d.schmitz@googlemail.com

* Correspondence: ligeng@cugb.edu.cn

Abstract

This study investigated twelve gem-quality color-change fluorite specimens exhibiting a purple–blue gradient from Nova Era, Brazil, using colorimetry, Raman spectroscopy, UV-Vis spectroscopy, photoluminescence spectroscopy, EDXRF, and DiamondView imaging to explore the relationship between color depth and coloration mechanism. Raman spectroscopy further revealed enhanced defect-related peaks in dark samples, indicating cumulative irradiation-induced lattice damage. EDXRF analysis revealed that the radioactive element Th was detected exclusively in dark samples, with the darkest specimen reaching 0.184 wt.% Th, confirming that long-term Th-induced irradiation is the primary driver of color deepening. In UV-Vis spectra, the ~583 nm plasmon resonance absorption band of calcium colloids progressively red-shifted and broadened with increasing color depth, indicating elevated colloid concentrations and enhanced aggregation that directly intensify body color. DiamondView fluorescence weakened with deepening color, attributed to the quenching effect of calcium colloids. Photoluminescence spectra showed that the Eu²⁺ emission peak intensified in dark samples, while the broad 700–900 nm emission band systematically blue-shifted, reflecting differential responses of luminescence centers to radiation damage. This study provides non-destructive spectroscopic criteria for the fluorite color-change mechanism without relying on micro-area compositional analysis, establishing an analytical paradigm linking color gradients with spectral characteristics.

Keywords: color-change fluorite; spectroscopy; color chromaticity; coloration mechanism; Nova Era; Brazil



Academic Editors: Teresa Pereira da Silva, Daniel P. S. De Oliveira and João Pedro Veiga

Received: 8 July 2026

Revised: 31 July 2026

Accepted: 3 August 2026

Published: 5 August 2026

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1. Introduction

Fluorite is a coordination-type fluoride mineral with the chemical composition CaF₂. It belongs to the cubic crystal system, possessing a structure characterized by high symmetry and substantial void spaces. In this structure, Ca can be isomorphously substituted by elements such as Ce, Y, Th, U, and Sr, while F can be replaced by Cl [1]. Pure fluorite is colorless; however, its coloration arises from several mechanisms: color centers formed by d–f transitions when rare-earth ions substitute at Ca²⁺ sites, calcium colloid color centers induced by radioactive irradiation, and coloration by organic matter [2–4]. Among these, color-center-related coloration is the most prevalent. The colors of fluorite encompass nearly all hues found in nature, with green, blue, purple, yellow, and colorless being common varieties. Furthermore, multiple color combinations may occur within a single fluorite crystal. Owing to its vibrant and diverse colors, fluorite has served as an important

material in the field of decoration and ornamentation from the Upper Paleolithic period to the present day [5].

Fluorite is also one of the few gemstones exhibiting pronounced photoreactivity, displaying fluorescence under ultraviolet and cathode-ray irradiation, with certain varieties additionally possessing phosphorescence and thermoluminescence properties. The photochromic effect refers to a reversible and distinct color change induced by external light excitation. Its essence lies in the charge transfer between valence-state changes in rare-earth ions and color centers, resulting in a reversible alteration of color. Common gemstones exhibiting photochromism include alexandrite, color-change garnet, color-change sapphire, color-change fluorite, and color-change sodalite. Among them, color-change garnet and color-change fluorite both belong to the cubic crystal system, with the garnet typically pertaining to the pyrope–spessartine series. Its color-change effect is primarily attributed to crystal field transitions of the transition metal ions Cr^{3+} and V^{3+} , presenting a marked contrast to the coloration mechanism of fluorite [6]. Previous studies have demonstrated that the purple–blue coloration of fluorite is jointly influenced by calcium colloid color centers and 2F^- color centers [7]. The photochromic shift from purple–blue to reddish-purple originates from the action of calcium colloid nanoparticles induced by the radioactive element thorium.

Existing research on fluorite has predominantly focused on geological deposit studies in countries such as the United States, Germany, France, India, the United Kingdom, and China [8–11], as well as comparative studies of fluorite of different colors. Precise investigations targeting different color gradients within the same hue series remain insufficient, and experimental analyses of gem-quality color-change fluorite are even scarcer. Color depth, an intuitive visual parameter, often contains critical information regarding the concentration of color centers, rare-earth element content, and defect evolution patterns. Furthermore, non-destructive testing constitutes the core methodology of gemological research, enabling the integrated acquisition of multiple types of key information—including structural, compositional, and spectral data—through various non-destructive techniques while fully preserving both the economic and esthetic value of the specimens.

Therefore, this study selected twelve gem-quality color-change fluorite samples from the Nova Era region of Brazil, cut into oval faceted stones, with the aim of establishing a spectroscopic fingerprint database for samples of varying color depth from the same locality and within the same hue series through the systematic and combined characterization using multiple non-destructive spectroscopic techniques, including Raman spectroscopy, infrared spectroscopy, UV-Vis spectroscopy, photoluminescence spectroscopy, and energy-dispersive X-ray fluorescence spectroscopy. This work not only provides a non-destructive spectroscopic criterion for the fluorite color-change mechanism that does not rely on high-precision micro-area compositional analysis, but also offers a research paradigm for investigating the correlation among color gradient, spectral characteristics, and coloration mechanism in gemology.

2. Geology

The color-change fluorite samples used in this study were sourced from the Nova Era region near the city of Itabira, Minas Gerais State, Brazil. This area is situated in south-eastern Brazil and tectonically belongs to an important segment of the Eastern Brazilian Pegmatite Province. This pegmatite province is renowned for hosting abundant granitic pegmatites associated with Proterozoic orogenesis and constitutes a significant source of gem-quality minerals in Brazil [12]. The geographic location and regional geological setting of the study area are presented in Figure 1.

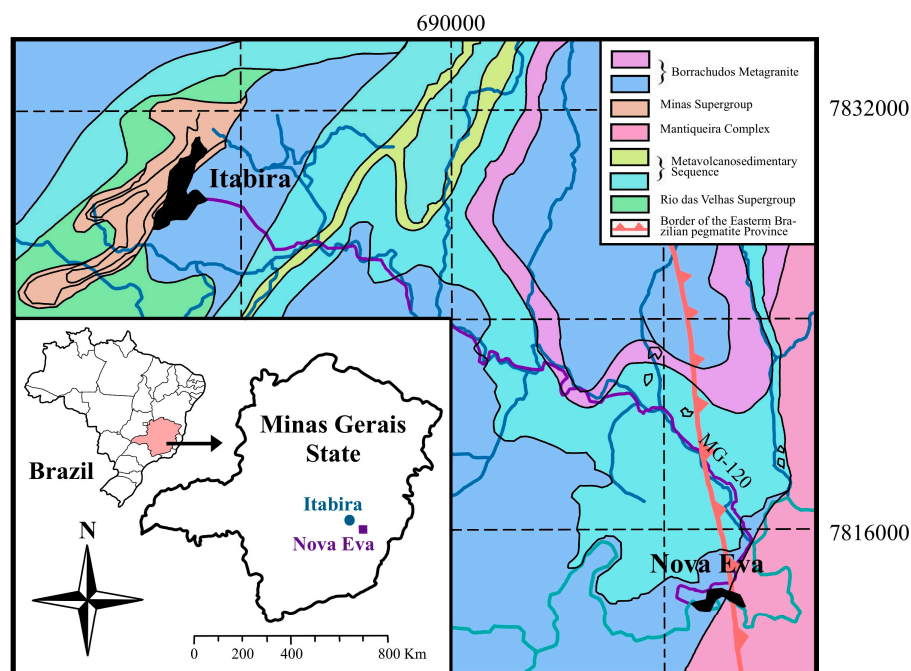


Figure 1. As the fluorite from the Nova Era area is sourced from small-scale artisanal mining sites and no mine-scale detailed geological map is available in the open literature, this figure is a schematic regional location map showing the outline of Minas Gerais State, the positions of towns including Nova Era and Itabira, and the distribution of pegmatites. Redrawn based on regional geological maps from the CPRM (Geological Survey of Brazil) and references [13–15].

Regionally, the Precambrian metamorphic sequences exposed in the Nova Era area primarily comprise schists, gneisses, and greenstone belt successions [16]. The pegmatite dikes in the area are relatively small in scale and typically intrude along the contact zones between schists and gneisses, occurring as veins or lenticular bodies with a predominant NE–SW strike, controlled by regional shear zones and fault systems. The pegmatites themselves are mainly composed of microcline, albite, quartz, and mica, and belong to the NYF-type (niobium–yttrium–fluorine) pegmatite family, characterized by their enrichment in fluorides. These pegmatites were formed during the Statherian period and represent the residual magmatic differentiation products of the Borrachudos Suite granite [17,18].

The fluorite in the Nova Era area occurs within the aforementioned pegmatite dikes, exhibiting purple to blue hues with high transparency that attains gem quality. The fluorite crystals are generally not large and are intergrown with typical pegmatite minerals such as K-feldspar, muscovite, and albite. On a global scale, pegmatite-hosted gem-quality fluorite is exceedingly rare, as the vast majority of fluorite deposits are of the hydrothermal vein type or stratabound type; the Nova Era area is thus one of the few known localities of gem-quality pegmatitic fluorite. Fluorite extraction in this area is predominantly conducted through small-scale artisanal mining, with very limited mining site dimensions, primarily including the Aleixo pegmatite, the Belomont mine, and the Cantá Galo mine [19].

The pegmatitic genesis exerts a decisive influence on the trace element composition of fluorite from this area. During the late-stage crystallization process, the pegmatitic melt becomes strongly enriched in incompatible elements, including rare earth elements, Y, Th, and U. The enrichment of elements such as Th, Y, Sm, and Yb revealed by EDXRF analysis in this study is a direct consequence of the long-term irradiation by natural radioactive elements within the pegmatite. These radioactive elements provide a sustained energy source for the formation of calcium colloid color centers in the fluorite lattice, which

constitutes the fundamental geological reason why fluorite from this locality exhibits an intense purple–blue hue and possesses photochromic properties.

3. Materials and Methods

3.1. Materials

This study examined 12 oval faceted color-change fluorite specimens from Brazil, which displayed a range of light to dark purple–blue hues within the same color series. The samples were numbered Y-1 to Y-12 according to their visual color intensity from lightest to darkest (Figure 2). This visual ordering was subsequently validated by the colorimetric analysis presented below, with the results demonstrating a deepening trend from Strong Blue (Y-1 to Y-4) through Vivid Blue (Y-5 to Y-11) to Strong Deep Blue (Y-12). Thus, the numbering reflects a color depth gradient corroborated by both visual observation and instrumental measurement. These samples exhibit a purple–blue hue ranging from light to dark within the same color series. No visible color zoning is observed in individual stones, and no inclusions are visible to the naked eye. All samples measure approximately 9 mm × 11 mm × 6 mm, and aside from cutting and polishing, none of the specimens have undergone any form of enhancement treatment.

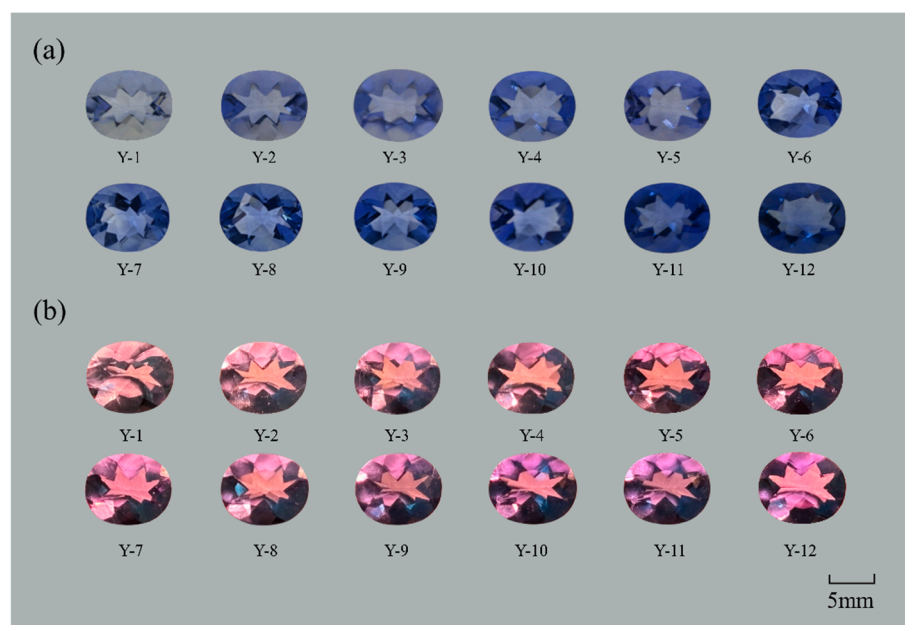


Figure 2. Twelve color-change fluorite samples: (a) color under daylight, (b) color under incandescent light.

3.2. Methods

3.2.1. Conventional Gemological Testing

Standard gemological properties were determined at the Gemological Laboratory of the School of Gemology, China University of Geosciences (Beijing). Instruments employed for testing included a Fable refractometer (Shenzhen, China), a custom-built hydrostatic balance based on a Mettler electronic balance (Mettler-Toledo Instruments (Shanghai) Co., Ltd., Shanghai, China), and a gemological microscope (Olympus BX51, Tokyo, Japan).

3.2.2. Colorimetric Analysis

The color parameters of the samples were measured at the Gemological Laboratory of the School of Gemology, China University of Geosciences (Beijing), using a LiuLab Multifunctional Spectrometer (LiuLab Inc., USA; distributed by Yaojia Technology Co., Ltd., China). This instrument is based on the CIELAB color space and calculates and outputs

a series of color parameters by measuring the spectral reflectance of the samples in the visible range (380–760 nm). During measurement, settings were configured in the software according to the actual shape and size of each sample, and an appropriate background was selected. After each measurement, the following colorimetric parameters were recorded: L^* (lightness), a , b , hue angle, saturation, as well as the average color grade and true color trade.

3.2.3. Raman Spectroscopy

At the Gemmology Laboratory of the School of Gemmology, China University of Geosciences (Beijing), a HORIBA HR-Evolution micro-Raman spectrometer (HORIBA Jobin Yvon, Villeneuve d'Ascq, France) is in use. It has a measurement range of $100\text{--}1000\text{ cm}^{-1}$, a resolution of 4 cm^{-1} , operates at 220 V and 10 A, and uses a 532 nm exciter.

3.2.4. Energy Dispersive X-Ray Fluorescence (EDXRF)

At the Gemmology Laboratory of the School of Gemology at China University of Geosciences (Beijing), semi-quantitative, non-destructive elemental analysis of samples was performed using an EDX-7000 energy-dispersive X-ray fluorescence spectrometer manufactured by Shimadzu Corporation (Kyoto, Japan). The instrument was operated under vacuum conditions with a voltage of 50 kV, a current of $1000\text{ }\mu\text{A}$, and a measurement aperture of 1 mm. Measurements were taken at two points on each of the twelve color-changing fluorite samples, and the average values were used for data analysis. The tested element range was Al–U and Na–Sc. The detection limits were at the ppm level for heavy elements and approximately 0.1 atomic percent for light elements. Data analysis and processing were performed using PCEDX software (PCEDX-Navi Version 2. 03) to remove sulfur values that were anomalous due to instrument error.

3.2.5. Fourier Transform Infrared (FTIR) Spectroscopy

Infrared spectroscopic analysis was performed using a TENSOR 27 Fourier transform infrared spectrometer (Bruker, Karlsruhe, Germany) at the School of Gemmology, China University of Geosciences (Beijing), employing the transmission method. Test conditions: transmission mode, 32 scans, resolution of 4 cm^{-1} , and a measurement range of $400\text{--}4000\text{ cm}^{-1}$.

3.2.6. UV-Visible (UV-Vis) Spectrophotometry

UV-Vis spectroscopic testing was performed using a UV-3600 UV-Vis spectrophotometer (Shimadzu Corporation, Kyoto, Japan) at the School of Gemmology, China University of Geosciences (Beijing). Prior to the experiment, a baseline correction for reflectance was performed using BaSO_4 . The scan speed was set to medium, the sampling interval to 1, the scan mode to single, the measurement method to reflectance, the time constant to 0.1 s, light source switching wavelength to 300.00 nm, detection unit to external (dual detector), detector switching wavelength to 850.00 nm, grating switching wavelength to 850.00 nm, S/R to reversed, beam mode to dual beam, and step correction was set to enabled.

3.2.7. DiamondView Fluorescence Imaging Analysis

The fluorescence characteristics of the samples were observed and imaged using a DiamondViewTM instrument (IIDGR, Marlow, UK) at the Gemological Laboratory of the School of Gemology, China University of Geosciences (Beijing). This instrument irradiates the sample surface with short-wave ultraviolet light to excite fluorescence emission, and the fluorescence images are captured by a built-in high-sensitivity camera. The experiments were conducted at room temperature. The samples were placed in the sample chamber, the focus was adjusted until the image was sharp, and fluorescence images were then

acquired. The fluorescence color, intensity, and distribution characteristics of the samples were observed and recorded.

3.2.8. Photoluminescence (PL) Spectroscopy

Photoluminescence spectroscopy measurements were performed at the Gemological Laboratory of the School of Gemology, China University of Geosciences (Beijing), using a Biaoqi Optoelectronics PL-Image photoluminescence spectrometer (Guangzhou BiaoQi Optoelectronics Technology Development Co., Ltd., Guangzhou, China). The instrument is equipped with a 405 nm laser as the excitation source, with a spectral acquisition range covering 200 to 1000 nm, and the laser power is continuously adjustable from 0 to 200 mW. The experiments were carried out at room temperature. The samples were placed on a loose-stone tray, the instrument parameters were adjusted until the signal was stable, and the photoluminescence spectral characteristics of the samples were recorded.

4. Results and Discussion

4.1. Basic Gemological Characteristics

The samples were numbered Y-1 to Y-12 according to their visually observed color from light to dark. They exhibited diverse color appearances under different light sources: purple–blue under daylight and reddish-purple under incandescent light. The basic gemological characteristics observed for the twelve samples are presented in Table 1. The refractive indices and relative densities of the samples are consistent with the standard values for natural fluorite. The differences in sample dimensions are not significant, and the cutting style is identical. All samples appeared completely dark under crossed polarizers and exhibited a light red to bright red color under the Chelsea color filter.

Table 1. Basic gemological data for each sample.

NUM.	Refractive Index	Specific Gravity	Internal Features	Chelsea Filter
Y-1	1.428	3.186	No obvious inclusions under the microscope.	Shallow red.
Y-2	1.431	3.183	No obvious inclusions under the microscope.	Red.
Y-3	1.430	3.191	No obvious inclusions under the microscope.	Red.
Y-4	1.427	3.177	No obvious inclusions under the microscope.	Bright red.
Y-5	1.427	3.194	Two-phase (gas–liquid) inclusions.	Red.
Y-6	1.428	3.182	Three-phase (gas–liquid–solid) inclusions	Bright red.
Y-7	1.430	3.189	Two-phase (gas–liquid) inclusions.	Red.
Y-8	1.429	3.201	No obvious inclusions under the microscope.	Red.
Y-9	1.431	3.194	No obvious inclusions under the microscope.	Bright red.
Y-10	1.431	3.189	No obvious inclusions under the microscope.	Bright red.
Y-11	1.432	3.202	No obvious inclusions under the microscope.	Bright red.
Y-12	1.430	3.193	Two-phase (gas–liquid) inclusions.	Bright red.

Regarding internal features, the gem-quality fluorite samples were eye-clean, and the majority of specimens showed no obvious inclusions under the microscope. Sample Y-7 exhibited multiple layers of veil-like two-phase (gas–liquid) inclusions occurring on the same plane under the microscope, as shown in Figure 3. For the inclusions occasionally observed in individual samples, this study attempted to perform Raman spectroscopic spot analysis without damaging the specimens. However, the inclusions were located at relatively deep positions within the samples, beyond the effective working distance of the instrument, and no usable spectral data could be obtained. The specific composition of these inclusions therefore remains to be investigated in further studies.

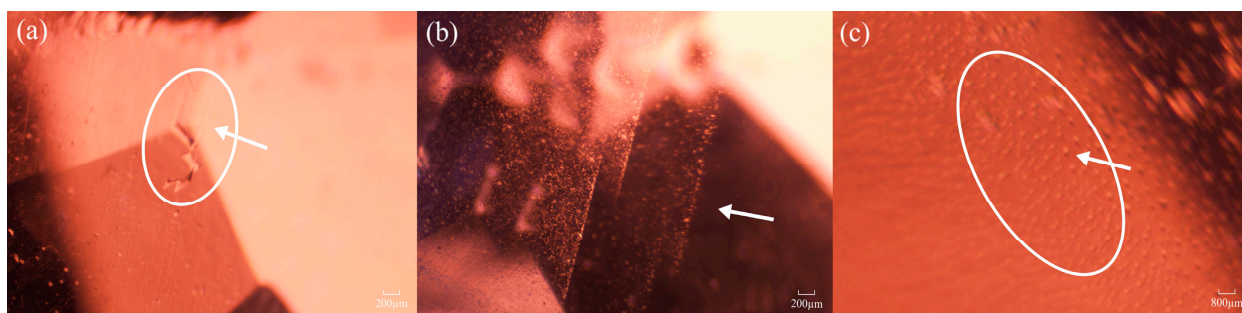


Figure 3. Photomicrographs of inclusions. (a) Inclusions with distinct boundary shapes in sample Y-6; (b) multiple layers of veil-like two-phase (gas–liquid) inclusions occurring on the same plane in sample Y-7; (c) widespread droplet-shaped inclusions.

4.2. Colorimetric Analysis

The colorimetric data for each sample are presented in Table 2, and the trends in lightness, hue angle, and saturation are shown in Figure 4. The L^* values exhibited a clear decreasing trend from Y-1 (48.21) to Y-12 (21.55), with rebounds observed in Y-7, Y-9, and Y-11, indicating the complexity of color perception and that color depth is not solely determined by lightness, presumably because the saturation is not yet sufficiently high to completely mask the contribution of lightness. The hue angle decreased from 263.91° to 258.19° . On the CIELAB color wheel, 270° represents pure blue, and a decrease in angle signifies a hue shift from blue toward bluish-purple, indicating that all samples fall within the blue to purple color range. Saturation (C^*) showed an upward trend from Y-1 (12.77) to Y-12 (17.03), indicating an overall increase in color vividness. Although Y-10 had the highest saturation, its lightness was relatively low, resulting in a dark visual appearance. The True Color Trade classification assigned the samples as follows: Strong Blue (Y-1 to Y-4), Vivid Blue (Y-5 to Y-11), and Strong Deep Blue (Y-12). The quantitative parameter trends and color grading derived from colorimetric analysis validated the color gradient ordering of the samples based on visual observation.

Table 2. Colorimetric data for each sample. In the CIELAB system, a^* represents the red/green coordinate; b^* represents the yellow/blue coordinate; and C^* represents the saturation.

NUM.	Lightness (L^*)	a^*	b^*	Hue Angle ($^\circ$)	Saturation (C^*)	Average Color Grade	True Color Trade
Y-1	48.21	−1.25	−11.74	263.91	12.77	Intense Blue	Strong Blue
Y-2	31.37	−0.95	−12.49	265.64	13.56	Intense Deep Blue	Strong Blue
Y-3	29.74	−0.45	−12.68	267.97	12.69	Intense Deep Blue	Strong Blue
Y-4	28.68	0.01	−13.17	270.05	14.26	Intense Deep Blue	Strong Blue
Y-5	27.4	−1.4	−14.32	264.42	15.57	Intense Deep Blue	Vivid Blue
Y-6	27.07	−1.41	−17.23	265.33	18.71	Intense Deep Blue	Vivid Blue
Y-7	27.6	−2.65	−15.23	260.13	16.73	Intense Deep Blue	Vivid Blue
Y-8	24.44	−2.09	−15.53	262.33	16.95	Intense Deep Blue	Vivid Blue
Y-9	28.63	−2.41	−16.65	261.78	18.21	Intense Deep Blue	Vivid Blue
Y-10	24.32	−2.25	−19.16	263.29	20.88	Strong Deep Blue	Vivid Blue
Y-11	26.74	−1.03	−15.34	266.15	16.64	Intense Deep Blue	Vivid Blue
Y-12	21.55	−2.95	−15.46	258.19	17.03	Intense Deep Blue	Strong Deep Blue

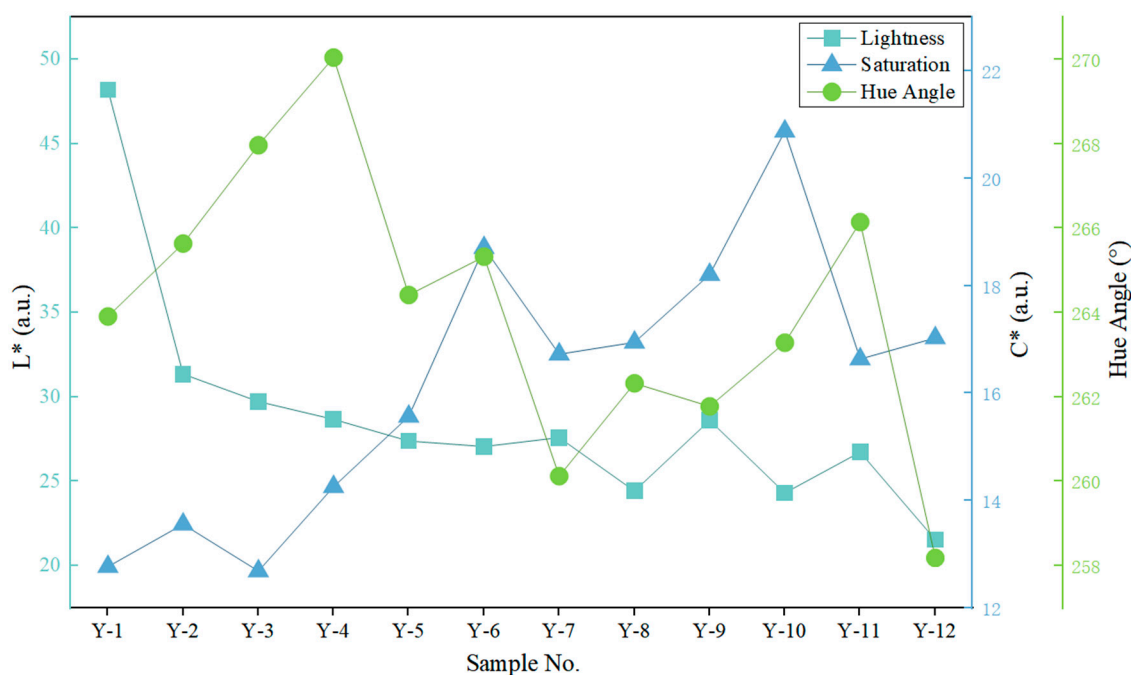


Figure 4. Line charts of lightness, hue angle, and saturation data for each sample.

4.3. Raman Spectroscopy

The Raman spectra in the $100\text{--}1000\text{ cm}^{-1}$ range are shown in Figure 5. No characteristic peaks were observed in the $1000\text{--}2000\text{ cm}^{-1}$ range, and this region is therefore omitted from presentation. All samples (Y-1 to Y-12) exhibited a sharp and high-intensity characteristic peak at 320 cm^{-1} , which is in full agreement with the typical principal band ($310\text{--}325\text{ cm}^{-1}$) of pure chemical reagent CaF_2 reported in previous studies, confirming that all samples are fluorite. In addition to the principal peak, peaks appearing near 227 and 486 cm^{-1} are associated with irradiation-induced lattice defects. The intensities of these defect-related peaks increased with increasing purple saturation [20]. Furthermore, two weaker peaks at 646 and 661 cm^{-1} can be attributed to photoluminescence bands of rare-earth ions, based on comparison with the energy level diagrams of various trivalent rare-earth ions in natural fluorite reported in previous studies [21,22].

Comparison of samples with different color gradients reveals that the dark-colored samples Y-12, Y-11, and Y-7 exhibit significantly higher intensities at all defect-related peaks, apart from the principal peak, than the light-colored samples. According to previous studies, unirradiated purple–blue fluorite displays only a single T_{2g} Raman-active band at 320 cm^{-1} , and with increasing irradiation dose, the intensities of other Raman peaks in the sample increase correspondingly [23,24]. It is therefore inferred that irradiation plays a significant role in inducing structural changes in dark-colored samples, i.e., color depth is positively correlated with the concentration of lattice defects.

4.4. EDXRF Compositional Analysis

The chemical compositions of all studied samples, expressed as the average of two measurements each determined by energy-dispersive X-ray fluorescence (EDXRF), are summarized in Table 3. Since the color-change effect of fluorite is directly related to the elements themselves rather than their oxides, all elemental contents are reported directly as single-element mass percentages (wt.%). Other elements not listed were either present at concentrations too low or could not be detected due to instrumental sensitivity limitations and spectral interferences. Given that fluorite has a Mohs hardness of 4, is relatively soft and brittle, and is therefore rarely fashioned into faceted gemstones—and because high-

quality fluorite cabochons are comparatively valuable—destructive techniques such as LA-ICP-MS were not employed in this study. Elemental characterization is based solely on non-destructive EDXRF results.

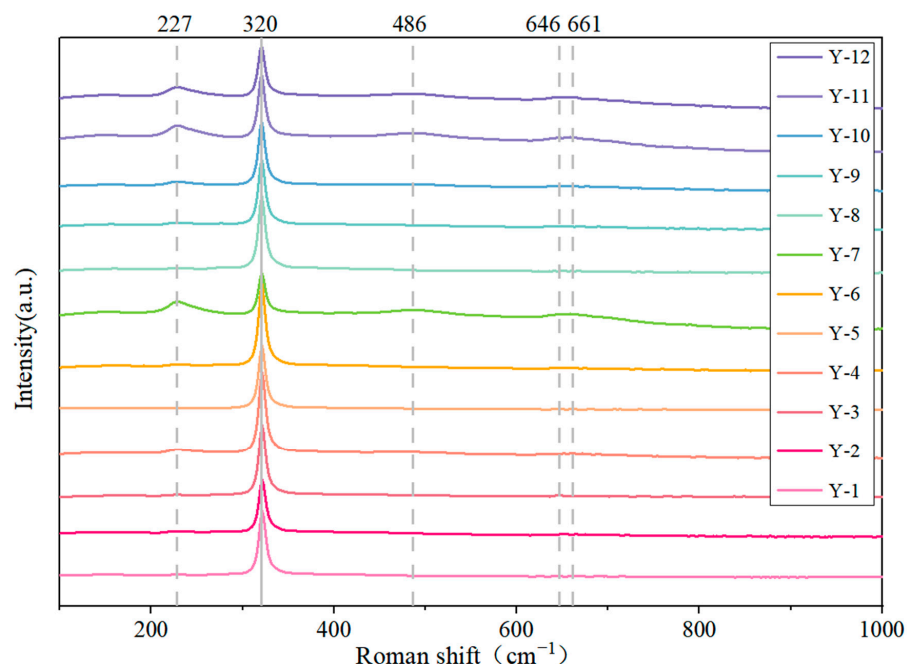


Figure 5. Raman spectra of all samples.

EDXRF semi-quantitative analysis revealed that all samples are predominantly composed of CaF_2 ($\text{Ca} > 99.2$ wt.%), with minor variations in major element composition among samples of different color depths. The total impurity element content is extremely low, and inhomogeneous distribution of rare-earth element (REE) concentrations exists within individual crystals. Fluorite specimens of identical color can reveal the presence of different REEs [25].

Previous LA-ICP-MS studies on blue to purple fluorite from the Ambadongar region of Gujarat, India, have shown that purple-toned fluorite samples contain extremely high Y contents, reaching 76.3 to 78.1 ppm, along with relatively high Eu contents of 0.79 to 0.89 ppm. Elements such as Gd, Tb, Dy, and Ho are also present at higher concentrations compared to fluorite of other colors. Blue fluorite is characterized by notably higher V content (ca. 3.2 ppm), whereas the average for other colored fluorites is only 1.2 ppm; Eu and Co are also relatively elevated [26]. As highly indicative trace components in fluorite, REEs (particularly Y) are often regarded as key factors in the coloration mechanism [27]. In the present study, Y was mostly below or near the detection limit in light-colored samples, yet was detected in all dark-colored samples except Y-11. Previous studies have indicated that when Y^{3+} ions substitute at Ca^{2+} sites, the charge difference necessitates accompanying charge-compensating defects such as interstitial F^- or cation vacancies, thereby significantly affecting the local lattice structure and promoting color center formation. The EDXRF semi-quantitative analysis in this study shows that Y is below the detection limit in light-colored samples (Y-1 to Y-3 and Y-5), whereas it is detected in dark-colored samples except for Y-11. Although the absolute concentrations are not high, the pervasive presence of Y at the dark end contrasts sharply with its complete absence at the light end, with the detection frequency exhibiting a somewhat positive correlation with color depth. This suggests that the activation or lattice release of Y under irradiation environments may be involved in regulating color center concentrations.

Table 3. EDXRF data for all samples. Hyphens indicate that the data is below the detection limit.

Sample	Ca	Si	Sr	K	Y	Th	Sm	Yb	Cu	Fe	Zn	V	Ni	Co	Mo	Nb	Ga	Ge	Rb	Au	Os	Se	As
Y-1	99.448	0.453	0.035	-	-	-	-	-	0.011	-	-	0.023	-	-	0.014	-	-	-	-	-	0.016	-	-
Y-2	99.534	0.422	-	-	-	-	-	-	0.012	0.010	-	-	-	-	0.010	0.012	-	-	-	-	-	-	-
Y-3	99.360	0.391	-	0.088	-	-	-	-	0.015	-	-	-	-	-	-	-	-	-	-	-	-	-	0.146
Y-4	99.478	0.371	0.015	0.087	0.013	-	-	-	0.014	-	-	-	-	-	0.022	-	-	-	-	-	-	-	-
Y-5	99.446	0.406	0.008	0.079	-	-	-	-	0.017	0.014	-	-	-	0.014	-	-	0.016	-	-	-	-	-	-
Y-6	99.591	0.318	-	-	0.008	-	-	-	0.012	-	-	0.032	-	-	-	0.039	-	-	-	-	-	-	-
Y-7	99.526	0.388	-	-	0.006	-	-	-	-	0.015	-	-	0.054	-	-	-	-	-	-	-	-	0.010	-
Y-8	99.396	0.372	-	0.089	0.022	0.015	0.031	-	-	-	0.026	-	0.049	-	-	-	-	-	-	-	-	-	-
Y-9	99.259	0.383	0.006	-	0.010	-	-	0.253	-	-	-	-	0.089	-	-	-	-	-	-	-	-	-	-
Y-10	99.468	0.386	-	-	0.008	-	-	-	0.016	-	-	-	0.045	-	-	-	-	-	0.077	-	-	-	-
Y-11	99.505	0.394	-	-	-	-	-	-	-	0.011	0.011	-	0.047	-	0.006	-	-	-	-	0.026	-	-	-
Y-12	99.261	0.370	-	0.085	0.021	0.184	-	-	-	-	-	-	0.048	-	-	0.006	-	0.024	-	-	-	-	-

The radioactive element Th was detected in the dark-colored sample Y-8 (0.015 wt.%) and the darkest sample Y-12 (0.184 wt.%), with the Th content of Y-12 being substantially higher than that of all other samples. This distribution pattern corresponds to the sample's color depth classification (Y-12 being the only one graded as Strong Deep Blue) and its lightness value ($L^* = 21.55$, the lowest in the entire set). This quantitative disparity indicates that, while Y-8 may represent an intermediate stage of radiation influence, Y-12 has experienced a substantially higher cumulative irradiation dose, resulting in its deepest coloration. It should be noted that color depth is a multifaceted attribute governed not solely by Th content, but also by factors such as irradiation duration, the spatial distribution of radioactive elements within the crystal, and the efficiency of color center formation and stabilization. Th is therefore regarded as a key contributing factor, particularly for the extreme depth of color observed in Y-12, though it is not the sole determinant of the entire color gradient. Purple fluorite generally contains higher concentrations of uranium and thorium compared to green fluorite [28], and when the Th content is sufficiently high, it drives the development of the deepest bluish-purple hue. This phenomenon is consistent with the geological setting of the Nova Era area, where the pegmatites are of the NYF type and naturally enriched in incompatible elements such as Th and U.

In addition to the aforementioned rare-earth elements, the anomalous distribution of certain transition metals and non-metallic elements is also noteworthy. Cu was detected only in samples of light to moderate depth (Y-1 to Y-6 and Y-10), with contents ranging from 0.011 wt.% to 0.017 wt.%, whereas it was below the detection limit in all dark-colored samples (Y-7 to Y-9, Y-11, and Y-12). This distribution pattern—present in lighter samples and absent in darker ones—suggests that Cu may exist as interstitial ions or complexes in the natural irradiation environment. With cumulative irradiation dose and increasing lattice defect density, Cu^{2+} may be reduced and precipitated as submicroscopic metallic clusters, or diffuse and migrate away from the detection volume along defect pathways, thereby causing its concentration in dark samples to fall below the instrumental detection limit. In contrast, Ni was not detected in any of the light-colored samples (Y-1 to Y-6), yet appeared consistently in all dark-colored samples from Y-7 onward, with contents ranging from 0.045 wt.% to 0.089 wt.%. This inverse Cu–Ni relationship across the color gradient indicates that the two elements exhibit different geochemical behaviors under irradiation conditions. Ni may enter the lattice via isomorphic substitution and subsequently be stabilized in the vicinity of defect sites due to irradiation-induced crystal field changes or charge compensation requirements, with its content increasing with greater radiation damage. Alternatively, Ni may have originally been hosted within micro-inclusions and subsequently released and dispersed into the lattice by high-energy irradiation, thus becoming detectable. As for As, it was anomalously enriched only in sample Y-3 (0.146 wt.%), a value far exceeding that of all other samples. Since As is not a typical isomorphic substituting element in fluorite, this isolated anomaly is more likely to indicate the accidental capture of minute arsenide mineral inclusions during the growth of the Y-3 crystal, representing a localized incidental event unrelated to the dominant mechanism governing the color gradient.

Furthermore, other rare-earth and transition metal elements were detected in some samples: 0.031 wt.% Sm was detected in Y-8, and the anomalously high Yb content in Y-9 (0.253 wt.%) may indicate the presence of REE-rich micro-inclusions. Uranium, however, was not detected above the detection limit in any of the samples in this study. Although the distribution of these minor elements does not exhibit a systematic pattern as pronounced as that of Th, their selective enrichment or anomalous values in dark-colored samples suggest that they may exert secondary modulating effects on the stability of color centers or luminescence behavior within the local lattice environment, yet are insufficient to account for the dominant direction of the color gradient [29].

Taken together, the consistency between the Th concentration gradient and color depth, along with the concomitant detection of REEs such as Y at the dark end, collectively point to Th-induced cumulative natural irradiation as the primary driving factor for color deepening, while other trace elements play more of a subsidiary or locally modulating role.

4.5. FTIR Spectroscopy

Fourier-transform infrared (FTIR) spectroscopy was performed on the samples using the reflection method, and the results are presented in Figure 6. Within the 500–4000 cm^{-1} wavenumber range, the spectra of all samples were highly similar, with only slight differences in intensity.

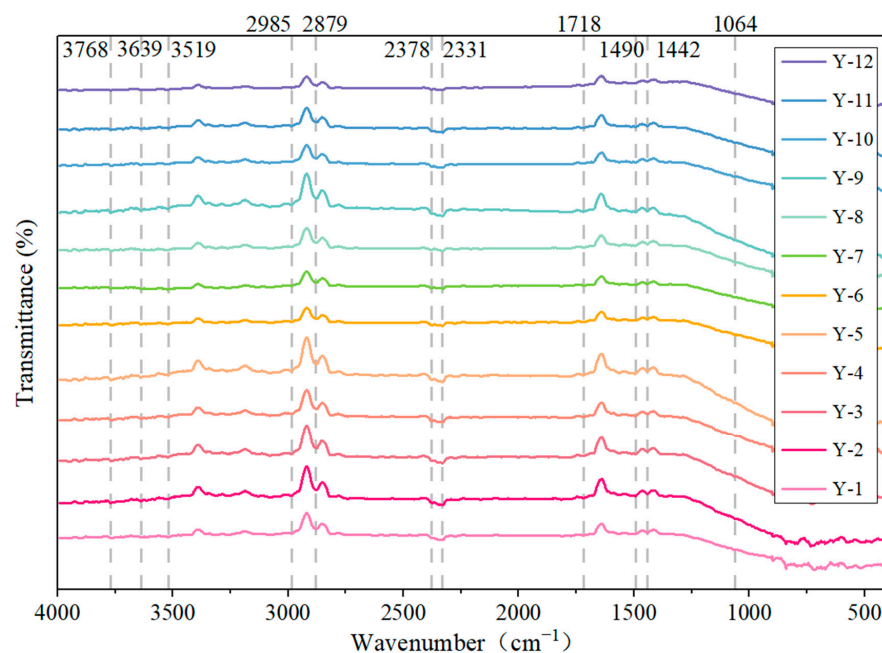


Figure 6. FTIR spectra of the samples. (Because the simultaneous display of all twelve samples renders the peak positions visually indistinct on the figure, the spectrum of each sample was displayed individually for peak identification during figure preparation, and the peak positions reported above were derived synthetically.).

The peak at 1064 cm^{-1} observed in all samples (Y-1 to Y-12) is a characteristic absorption peak of calcium fluoride. The attributions of the remaining specific peaks are given in Table 4. All samples contain carbonate inclusions, aqueous fluid inclusions, CO_2 gas inclusions, and trace organic matter, indicating that the samples were formed in an ore-forming fluid environment enriched in the relevant components.

Table 4. Attribution of infrared peak positions.

Infrared Peak Position (cm^{-1})	Previous Literature (cm^{-1})	Peak Interpretation
1064	~1080	Characteristic peak of calcium fluoride
1442, 1490	~1450	Asymmetric stretching vibration (ν_3) of CO_3^{2-}
1718	~1643	Bending vibration of H–O–H bonds in crystalline water or adsorbed water
2331, 2378	~2330 and 2360	Vibrations of carbon dioxide (CO_2); these two peaks may correspond to different isotopic species of the CO_2 molecule or different vibrational modes
2879, 2985	2852 and 2928	C–H stretching vibrations of organic matter, possibly associated with surface adsorption or fluid inclusions
3519, 3639, 3768	3200–3700	Stretching vibrations of structural water, adsorbed water, or hydroxyl (OH^-)

4.6. UV-Vis Spectral Analysis

The UV-Vis spectral results are presented in Figure 7. All samples (Y-1 to Y-12) exhibit similar spectral features, characterized by a distinct broad absorption band centered at approximately 583 nm [30]. This absorption band is attributed to the plasmon resonance absorption of calcium colloid nanoparticles, which gives rise to the purple–blue coloration of fluorite. This is consistent with the 560–580 nm absorption feature reported in previous studies. When fluorite or the surrounding rocks are subjected to prolonged exposure to radioactive elements, F^- ions lose electrons, while Ca^{2+} ions capture these electrons to form calcium colloids.

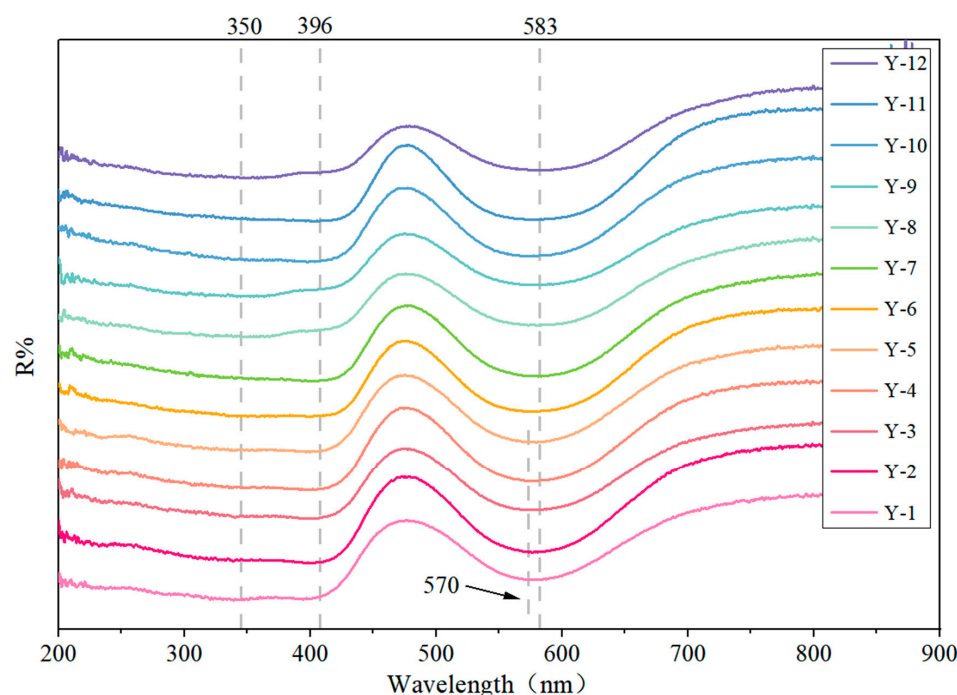


Figure 7. UV-Vis spectra of the samples.

Comparison of samples with different color gradients reveals that the light-colored samples Y-1 and Y-2 exhibit a relatively high-intensity absorption peak near 570 nm, whereas the absorption bands of the dark-colored samples Y-3 to Y-12 gradually broaden, with the peak positions systematically red-shifting to approximately 583 nm and the absorption profiles tending to flatten. This peak red-shift and band broadening indicate that with increasing cumulative radioactive irradiation, the concentration of calcium colloid nanoparticles precipitated in the fluorite lattice continuously rises and aggregation occurs, inducing strong broadband absorption and light scattering, thereby leading to significant deepening of the body color. The absorption bands at 350 and 396 nm in the near-ultraviolet to violet region are also consistent with the peak positions at 335 and 400 nm reported in previous studies [31]. The transmission windows in the blue-green and red regions, together with the localized absorption peak in the yellow region, cause the samples to reflect blue light under daylight (rich in blue light), exhibiting a purple–blue color, and to transmit red light under incandescent light (rich in red light), exhibiting a reddish-purple color. This transmission window distribution pattern is highly consistent with the alexandrite effect and the spectral characteristics of other color-change gemstones, providing direct spectroscopic evidence for the color-change phenomenon. Correspondingly, the samples display a bright red transmitted color under the Chelsea color filter, further confirming their high transmittance in the red spectral region.

4.7. Luminescence

4.7.1. Fluorescence

All samples displayed blue fluorescence under DiamondView (Figure 8). The blue fluorescence is primarily attributed to the $4f^7 \rightarrow 4f^65d^1$ transition of Eu^{2+} [32]. Excluding the influence of obvious reflective areas at the center of the images, the lighter-colored samples Y-1 to Y-3 exhibited strong fluorescence intensity, whereas the fluorescence of samples Y-6 to Y-12 was notably weaker, with the darkest sample, Y-12, displaying the lowest fluorescence intensity, directly demonstrating a negative correlation between fluorescence intensity and color gradient. This phenomenon can be attributed to the fact that under high-energy short-wave ultraviolet excitation, the excited-state energy must be transferred through the lattice before reaching the Eu^{2+} luminescence centers. In dark-colored samples, the high concentration of calcium colloid nanoparticles and abundant structural defects serve as effective non-radiative recombination centers, preferentially capturing the excited-state energy during the energy transfer process and dissipating it in the form of lattice vibrations. Consequently, the excitation energy actually received by Eu^{2+} is substantially reduced, leading to a systematic decrease in the blue fluorescence emission efficiency with increasing body color depth [33,34].

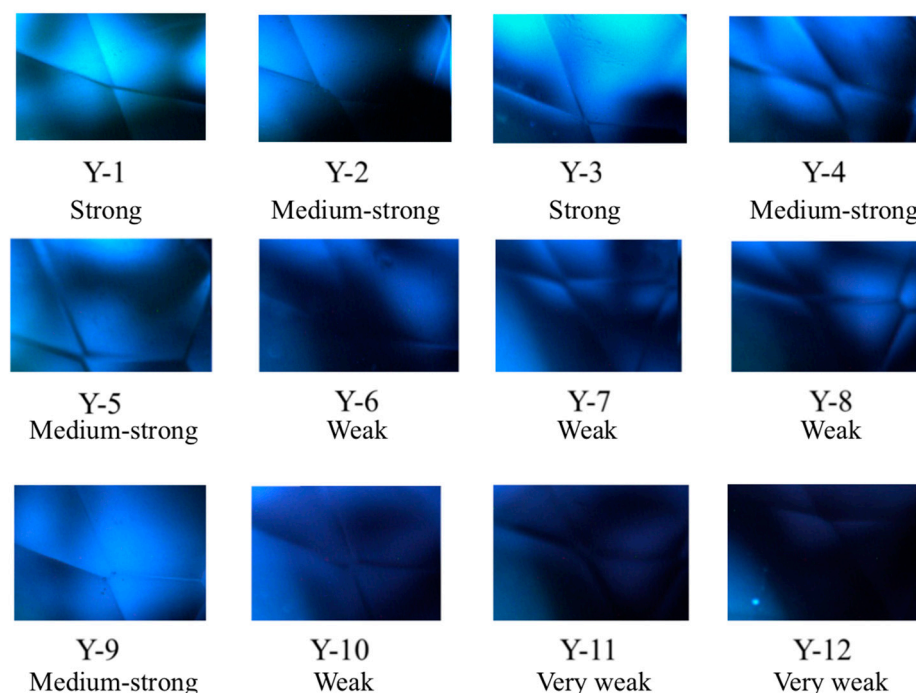


Figure 8. Images captured under DiamondView.

4.7.2. Photoluminescence (PL)

The 405 nm photoluminescence spectra of all studied samples exhibit similar characteristics (Figure 9). A distinct peak is observed at 424 nm in all samples, corresponding to the characteristic luminescence of the rare-earth element Eu^{2+} . The emitted light falls within the violet-blue region of the visible spectrum [35]. Sample Y-12 exhibits the highest peak intensity, followed by Y-7 and Y-10, while Y-1 to Y-5 display weaker intensities. Contrary to the trend observed under DiamondView, where fluorescence intensity decreases with increasing color depth, the intensity of the Eu^{2+} emission peak at 424 nm in the PL spectra is higher in the dark-colored samples. This phenomenon arises from a fundamental difference in excitation mechanisms. The 405 nm wavelength corresponds to a characteristic excitation absorption band of Eu^{2+} , enabling direct and selective excitation of Eu^{2+} ions without relying on energy transfer pathways through other defects or calcium colloid nanoparticles.

in the lattice. Therefore, the PL spectra reflect information concerning the concentration of Eu^{2+} itself and its local crystal field environment—the enhanced Eu^{2+} emission in dark-colored samples may indicate a higher absolute concentration or irradiation-induced partial valence reduction from Eu^{3+} to Eu^{2+} [36–41]. In contrast, DiamondView employs short-wave ultraviolet excitation that involves excitation energy transfer processes throughout the entire lattice, and the overall fluorescence efficiency is governed by the quenching effect of defects and calcium colloids. These two techniques reveal the occurrence state of Eu^{2+} in dark-colored samples from different dimensions: although its absolute content or emission activity may increase with the degree of irradiation, the abundant calcium colloids and defects generated concomitantly effectively quench the overall fluorescence emission under non-selective excitation conditions.

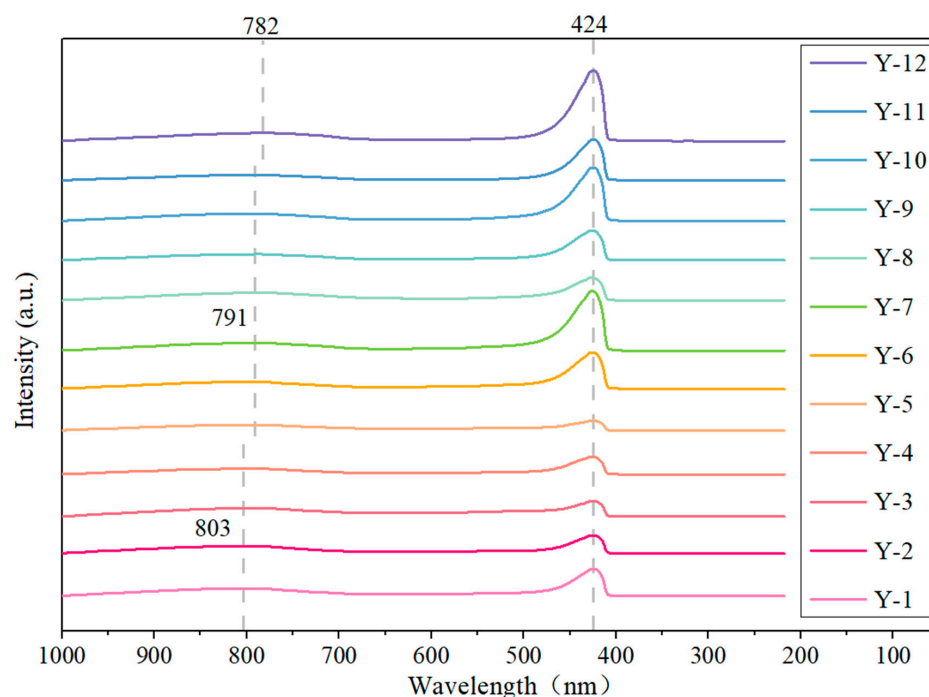


Figure 9. PL-IMAGE photoluminescence spectra of the samples.

Furthermore, all samples exhibit a broad emission band in the 700–900 nm range, spanning the deep-red to near-infrared region and representing a typical infrared luminescence band. A systematic, albeit moderate, blue-shift in the peak maximum is observed across samples of different color depth: the peak maximum is located at approximately 803 nm for samples Y-1 to Y-5, at approximately 791 nm for Y-6 to Y-11, and at 782 nm for Y-12. It is inferred that with increasing color depth, the lattice environment of the luminescence centers responsible for this broadband emission undergoes systematic contraction or stress changes, leading to an increase in energy-level spacing and a consequent shift in the emitted light wavelength toward the shorter-wavelength direction (from the near-infrared toward the deep-red end). From the perspective of individual luminescence centers, this phenomenon provides continuously graded spectroscopic evidence supporting the conclusion that radiation damage is more severe in darker samples.

Integrating the conclusions drawn from the various experimental data, it can be inferred that the color depth gradient of Brazilian color-change fluorite is essentially caused by differences in the cumulative degree of natural radioactive irradiation. These differences not only lead to variations in the concentration of color centers such as calcium colloids, thereby affecting the UV-Vis spectra and body color, but also systematically alter the concentration of lattice defects, which in turn influence the Raman spectra and DiamondView

fluorescence, and even affect the luminescence efficiency of specific rare-earth ions while causing changes in the energy-level structure of the 700–900 nm emission peak.

5. Conclusions

This study systematically characterized twelve color-change fluorite specimens exhibiting a purple–blue gradient from pegmatite-type deposits in Nova Era, Brazil, using multiple non-destructive spectroscopic techniques, revealing the intrinsic link between color depth and coloration mechanism. Colorimetric analysis quantitatively confirmed a continuous trend from light purplish-blue to deep bluish-purple, marked by decreasing lightness and increasing saturation, providing a reliable visual baseline for subsequent spectroscopic and compositional comparisons. Raman spectroscopy further showed that defect-related peaks at 227 and 486 cm^{-1} were significantly stronger in darker samples, indicating that color deepening is accompanied by a systematic increase in lattice defect concentration, and suggesting that natural irradiation played a dominant role in structural evolution.

This inference was critically validated by compositional analysis: the radioactive element Th exceeded the detection limit only in dark-colored samples, with the darkest specimen Y-12 reaching 0.184 wt.%, far higher than all others, confirming that long-term Th-induced irradiation is the key driver of defect accumulation and color deepening. The trace element distribution patterns provide further geochemical support for this irradiation-driven mechanism. Beyond the gradient trends of Th and Y, Cu was detected only in light to moderately dark samples and fell below the detection limit in darker ones, whereas Ni was found exclusively in dark-colored samples at 0.045–0.089 wt.%. It is inferred that the natural irradiation environment not only generated calcium colloid color centers and lattice defects, but also drove the migration, valence-state transformation, or reconfiguration of trace element occurrence states within the lattice.

UV-Vis spectroscopy provided direct colorimetric evidence for the irradiation mechanism described above. All samples exhibited a broad absorption band centered at ~583 nm, attributed to the plasmon resonance absorption of calcium colloid nanoparticles, which constitutes the spectroscopic origin of the purple–blue hue and the color-change phenomenon. With increasing color depth, this absorption band underwent systematic red-shifting and pronounced broadening, reflecting elevated calcium colloid concentration and enhanced particle aggregation, which intensified visible-light scattering and absorption, thereby deepening the body color. This continuous variation is highly consistent with the Raman defect peak intensities and Th content distribution, collectively pointing to irradiation dose differences as the decisive factor governing the color gradient. Although FTIR spectroscopy revealed that the samples universally contain carbonate, aqueous fluid, and organic matter inclusions, these components are uniformly distributed across all samples and exhibit no systematic correlation with color depth, thus ruling them out as the dominant coloration factor.

The luminescence behavior of the samples further corroborates the cumulative effect of irradiation damage from an independent perspective. DiamondView fluorescence imaging showed that under short-wave UV excitation, light-colored samples emitted strong blue fluorescence, whereas dark-colored samples displayed markedly diminished fluorescence, with fluorescence intensity exhibiting a clear negative correlation with color depth. This quenching effect is attributed to the high concentration of calcium colloid nanoparticles and structural defects acting as non-radiative recombination centers during the excitation energy transfer process. In contrast, under 405 nm excitation in PL spectroscopy, the characteristic Eu^{2+} emission peak (~424 nm) was more intense in dark-colored samples. This is because the 405 nm laser selectively and directly excites Eu^{2+} ions, bypassing the energy competition pathways involving defects and calcium colloids, thereby reflecting an

elevated intrinsic Eu^{2+} concentration or irradiation-induced valence reduction from Eu^{3+} to Eu^{2+} . These two techniques, operating under different excitation modes, reveal the same physical reality: cumulative irradiation simultaneously increases the absolute content or activity of rare-earth ions while generating more quenching centers, producing contrasting yet intrinsically consistent luminescence trends under different experimental conditions.

In summary, the color depth gradient of Brazilian color-change fluorite is not caused by differences in major element composition or inclusion types, but rather by varying degrees of cumulative long-term irradiation induced by the natural radioactive element Th, which systematically regulates the concentration of calcium colloid color centers, the density of lattice defects, and the local environment and luminescence behavior of rare-earth ions. However, although the consistent trend between Th content and color depth supports the irradiation-induced coloration interpretation, establishing a rigorous causal relationship still requires quantitative validation through higher-sensitivity techniques such as LA-ICP-MS on a larger sample set. Given that gem-quality faceted specimens are extremely precious and irreplaceable, such destructive analyses could not be performed in the present study. Should rough material become available or minimally destructive sampling be permitted in the future, LA-ICP-MS analysis could be employed to complement the non-destructive spectroscopic results provided herein. This study not only provides non-destructive spectroscopic criteria for the photochromic mechanism of fluorite without reliance on micro-area compositional analysis, but also establishes an analytical paradigm linking color gradient, spectral characteristics, and coloration mechanism, offering a reference framework for the genesis studies of similar gem materials.

Author Contributions: Conceptualization, N.J. and G.L.; methodology, N.J.; software, N.J.; validation, N.J.; formal analysis, N.J.; investigation, N.J. and G.L.; resources, F.D.S.; data curation, N.J.; writing—original draft preparation, N.J.; writing—review and editing, G.L.; visualization, N.J.; supervision, G.L.; project administration, G.L. and F.D.S.; funding acquisition, F.D.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The original contributions presented in the study are included in the article; further inquiries can be directed to the corresponding author.

Acknowledgments: The authors are grateful to the School of Gemmology, China University of Geosciences (Beijing), for their help with the preparation of data in this paper.

Conflicts of Interest: Fabian Dietmar Schmitz is an employee of Rhein Main Gem Consulting, Mainz, Germany. The paper reflects the views of the scientists and not the company.

References

1. Ye, X.M.; Bai, F. Spectral Characteristics, Rare Earth Elements, and Ore-Forming Fluid Constrains on the Origin of Fluorite Deposit in Nanlishu, Jilin Province, China. *Minerals* **2022**, *12*, 1195. [\[CrossRef\]](#)
2. Bill, H.; Calas, G. Color centers, associated rare-earth ions and the origin of coloration in natural fluorites. *Phys. Chem. Miner.* **1978**, *3*, 117–131. [\[CrossRef\]](#)
3. Ronchi, L.H.; Touray, J.C.; Michard, A.; Dardenne, M.A. The Ribeira fluorite district, southern Brazil. *Miner. Depos.* **1993**, *28*, 240–252. [\[CrossRef\]](#)
4. Mackenzie, K.J.D.; Green, J.M. The cause of coloration in Derbyshire Blue John banded fluorite and other blue banded fluorites. *Mineral. Mag.* **1971**, *38*, 459–470. [\[CrossRef\]](#)
5. Goemaere, É.; Vanmontfort, B.; Golitko, M.; Delhoofs, H.; Garrido-Cordero, J.Á.; Odriozola, C.P.; Pelucchi, S.; Reinert, M.; Ritoók, A.; Ruppené, V.; et al. Fluorite from the Paleolithic to the Present Day: A Common Heritage of Humanity. *Geoheritage* **2026**, *18*, 2. [\[CrossRef\]](#)

6. Liu, C.H.; Chen, C.Y.; Shao, T.; Li, Z.B.; Andy, H.S. UV-Vis Absorption Spectra and 3D Fluorescence Spectra Study of Color-Change Garnet with Red Fluorescence. *Spectrosc. Spectr. Anal.* **2020**, *40*, 2148.
7. Liu, Y.; Guo, Q.F.; Liu, L.Y.; Zhang, S.X.; Li, Q.L.; Liao, L.B. Comparative Study on Gemological and Mineralogical Characteristics and Coloration Mechanism of Four Color Types of Fluorite. *Crystals* **2023**, *13*, 75. [\[CrossRef\]](#)
8. Sasmaz, A.; Kryuchenko, N.; Zhovinsky, E.; Suyarko, V.; Konakci, N.; Akgul, B. Major, trace and rare earth element (REE) geochemistry of different colored fluorites in the Bobrynets region, Ukraine. *Ore Geol. Rev.* **2018**, *102*, 338–350. [\[CrossRef\]](#)
9. Alipour, S.; Abedini, A.; Talaie, B. Geochemical characteristics of the Qahr-Abad fluorite deposit, southeast of Saqqez, western Iran. *Arab. J. Geosci.* **2015**, *8*, 7309–7320. [\[CrossRef\]](#)
10. Sanchez, V.; Cardellach, E.; Corbella, M. Variability in fluid sources in the fluorite deposits from Asturias (N Spain): Further evidences from REE, radiogenic (Sr, Sm, Nd) and stable (S, C, O) isotope data. *Ore Geol. Rev. J. Compr. Stud. Ore Genes. Ore Explor.* **2010**, *37*, 87–100. [\[CrossRef\]](#)
11. Rossi, D.Q.; Endo, I.; Gabriel, E.G. Structural framework of the iron district of Itabira, Iron Quadrangle, Minas Gerais. *REM-Int. Eng. J.* **2019**, *72*, 39–45. [\[CrossRef\]](#)
12. Travassos, L.E.P.; Teixeira, R.C.; Ferreira, A.C.; Oliveira, I.F.G.; Pereira, I.E.O. Geoheritage, Myth, and Perception: Sacred Caves and Landscapes in Minas Gerais, Brazil. *Geoheritage* **2026**, *18*, 1. [\[CrossRef\]](#)
13. Morteani, G.; Preinfalk, C.; Horn, A.H. Classification and mineralization potential of the pegmatites of the Eastern Brazilian Pegmatite Province. *Miner. Depos.* **2000**, *35*, 638–655. [\[CrossRef\]](#)
14. Jordt-Evangelista, H.; Lana, C.; Delgado, C.E.R.; Viana, D.J. Age of the emerald mineralization from the Itabira-Nova Era District, Minas Gerais, Brazil, based on LA-ICP-MS geochronology of cogenetic titanite. *Braz. J. Geol.* **2018**, *46*, 427–437.
15. Preinfalk, C.; Kostitsyn, Y.; Morteani, G. The pegmatites of the Nova Era-Itabira-Ferros pegmatite district and the emerald mineralisation of Capoeirana and Belmont (Minas Gerais, Brazil): Geochemistry and Rb-Sr dating. *Crítica* **2018**, *50*, 867.
16. de Souza, J.L.; Mendes, J.C.; da Silveira Bello, R.M.; Svisero, D.P.; Valarelli, J.V. Petrographic and microthermometrical studies of emeralds in the ‘Garimpo’ of Capoeirana, Nova Era, Minas Gerais State, Brazil. *Miner. Depos.* **1992**, *27*, 161–168. [\[CrossRef\]](#)
17. Gonçalves, J.A.C.; Pereira, P.H.R.; Almeida, M.S.L. Characterization of the aquifer systems of the Itabira Iron district, Minas Gerais. *Águas Subterrâneas* **2021**, *35*, 1. [\[CrossRef\]](#)
18. Leme, E.S.V.C.; Porto, C.G.; Nascimento, J.A.C.; Abram, M.B.; de Sousa, S.Q.; de Oliveira, J.P.P.; Pufahl, P.K. The role of hydrothermal enrichment in the Pratápolis sedimentary phosphorite deposit, Minas Gerais, Brazil. *J. South Am. Earth Sci.* **2026**, *174*, 105998. [\[CrossRef\]](#)
19. Cavalcanti, J.A.D.; da Silva, M.S.; Schobbenhaus, C.; Atencio, D.; de Lima, H.M. Geoconservation of geological and mining heritage related to banded iron formation of Itabira Group, Quadrilátero Ferrífero, Minas Gerais, Brazil: A challenging issue. *Int. J. Geoheritage Parks* **2023**, *11*, 118–148. [\[CrossRef\]](#)
20. Yu, Z.S.; Zhang, F.F.; Shu, Q.H.; Liu, J.Y.; Shi, Q.H.; He, Z.F.; Niu, X.D.; Zhao, Y. Typomorphic and geochemical signatures of multi-colored fluorite: A proxy for magmatic-hydrothermal W-Sn and Mo systems. *J. Geochem. Explor.* **2026**, *285*, 108034. [\[CrossRef\]](#)
21. Čermáková, Z.; Bezdička, P.; Němec, I.; Hradilová, J.; Šrein, V.; Blažek, J.; Hradil, D. Naturally irradiated fluorite as a historic violet pigment: Raman spectroscopic and X-ray diffraction study. *J. Raman Spectrosc.* **2015**, *46*, 236–243. [\[CrossRef\]](#)
22. Alencar, I.; Ruiz-Fuertes, J.; Schwartz, K.; Trautmann, C.; Bayarjargal, L.; Haussühl, E.; Winkler, B. Irradiation effects in CaF₂ probed by Raman scattering. *J. Raman Spectrosc.* **2016**, *47*, 978–983. [\[CrossRef\]](#)
23. Srivastava, R.; Lauer, H.V., Jr.; Chase, L.L.; Bron, W.E. Raman frequencies of fluorite crystals. *Phys. Lett. A* **1971**, *36*, 333–334. [\[CrossRef\]](#)
24. Keramidas, V.G.; White, W.B. Raman spectra of oxides with the fluorite structure. *J. Chem. Phys.* **1973**, *59*, 1561–1562. [\[CrossRef\]](#)
25. Santos, R.A.; Silva, A.C.; Neto, A.B.S.; Cruz, A.R.P.; Melo, G.T.P.; Leite, L.M.S.A.; Roberto, M.R.S.; Asfora, V.K.; Oliveira, C.N.P.; Suárez-Rojas, A.; et al. Thermoluminescent emission spectroscopy of fluorite. *J. Lumin.* **2025**, *286*, 121450. [\[CrossRef\]](#)
26. Almohammed, A.H.; Bhui, U.K.; Ray, D.; Shukla, A.D.; Madhavan, N. Spectroscopic characterization of fluorite of Amba Dongar, Gujarat, India: Linking chemical composition with color. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2024**, *318*, 124464. [\[CrossRef\]](#) [\[PubMed\]](#)
27. Cao, J.C. Geochemical Characteristics of Rare Earth Elements in Epithermal Vein Fluorite Deposits from South China. *Geochimica* **1995**, *24*, 225–234. (In Chinese)
28. Huang, J.C.; Peng, J.T. Rare earth element (REE) geochemistry of different colored fluorites from the Baoshan Cu–Pb–Zn deposit, Southern Hunan, South China. *Acta Geochim.* **2022**, *41*, 419–433. [\[CrossRef\]](#)
29. Zhao, W.G.; Li, Z.H.; Fan, M.S.; Pan, J.Y. Geology, fluid inclusion and fluorite geochemistry constraints on the genesis of the large-scale Guancun fluorite deposit, Zhejiang Province, Southeast China. *Ore Geol. Rev.* **2026**, *189*, 107122. [\[CrossRef\]](#)
30. Jiang, N.; Li, G.; Schmitz, F.D. Chromogenic and Chromotropic Mechanisms of Color-Changing Fluorite from the Huanggangliang Area, Inner Mongolia. *Appl. Sci.* **2026**, *16*, 5842. [\[CrossRef\]](#)
31. Sturman, N.; Al-Alawi, A. Color-change fluorite. *Gems Gemol.* **2006**, *42*, 173–174.

32. Przibram, K. Fluorescence of Fluorite and the Bivalent Europium Ion. *Nature* **1935**, *135*, 100. [[CrossRef](#)]
33. Gaft, M.; Nagli, L.; Cheskis, D.; Raichlin, Y.; Waychunas, G.A.; Rossman, G.R.; Panczer, G. Red photoluminescence and purple color of naturally irradiated fluorite. *Phys. Chem. Miner.* **2020**, *47*, 11. [[CrossRef](#)]
34. Ge, X.; Guo, Q.F.; Wang, Q.Q.; Li, T.; Liao, L.B. Mineralogical Characteristics and Luminescent Properties of Natural Fluorite with Three Different Colors. *Materials* **2022**, *15*, 1983–1996. [[CrossRef](#)] [[PubMed](#)]
35. Sidike, A.; Lee, K.; Kusachi, I.; Yamashita, N. Photoluminescence properties of a natural fluorite. *J. Mineral. Petrol. Sci.* **2000**, *95*, 228–235. [[CrossRef](#)]
36. Yan, Q.C.; Liu, Z.Y.; Guo, Y. Study on Fluorescence Properties of Green-Blue Apatite. *Crystals* **2022**, *12*, 866. [[CrossRef](#)]
37. Przibram, K. Absorption Bands and Electron Transitions in Coloured Fluorites. *Nature* **1938**, *141*, 970. [[CrossRef](#)]
38. Wang, C.H.; Chen, X.T.; Luo, X.; Zhao, J.J.; Qiao, X.S.; Liu, Y.; Fan, X.P.; Qian, G.D.; Zhang, X.H.; Han, G.R. Stabilization of Divalent Eu^{2+} in Fluorosilicate Glass-Ceramics via Lattice Site Substitution. *RSC Adv.* **2018**, *8*, 34536–34542. [[CrossRef](#)] [[PubMed](#)]
39. Kohara, Y.; Okada, G.; Tsuyumoto, I.; Kusano, E.; Nanto, H. Radiation-Induced Reduction of Eu^{3+} Doped in SrAl_2O_4 . *Mater. Lett.* **2021**, *303*, 130502. [[CrossRef](#)]
40. Pandey, C.; Dhopte, S.M.; Muthal, P.L.; Kondawar, V.K.; Moharil, S.V. Eu^{3+} harr Eu^{2+} Redox Reactions in Bulk and Nano CaF_2 : Eu. *Radiat. Eff. Defects Solids* **2007**, *162*, 651–658.
41. Malchukova, E.; Boizot, B. Reduction of Eu^{3+} to Eu^{2+} in Aluminoborosilicate Glasses under Ionizing Radiation. *Mater. Res. Bull.* **2010**, *45*, 1299–1303. [[CrossRef](#)]

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