

# Analyzing Optical Properties of Natural Fluorite Crystals: A Comprehensive Investigation

## Maryam Shakooei<sup>1</sup>, M Mahdi Shahidi<sup>2,\*</sup>, Arezoo Abedi<sup>1</sup> and Mona Mehrabani<sup>3</sup>

<sup>1</sup>Faculty of Mining, Petroleum and Geophysics, Shahrood University of Technology, Shahrood, Iran

<sup>2</sup> Nanosciences African Network (NANOAFNET), IThemba LABS-National Research Foundation, 1 Old Faure Road, Somerset West, 7129, PO Box 722, Somerset West, Western Cape, South Africa

<sup>3</sup>Department of Physics, Shahrood University of Technology, Shahrood, Iran

\***Corresponding Author:** M Mahdi Shahidi Nanosciences African Network (NANOAFNET), IThemba LABS-National Research Foundation, 1 Old Faure Road, Somerset West, 7129, PO Box 722, Somerset West, Western Cape, South Africa E-mail: mmahdishahidi@semnan.ac.ir

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# Abstract

Fluorite, a primary fluorine mineral, plays a crucial role in various chemical and manufacturing processes. In this study focuses on the structural and optical characteristics of four natural fluorite crystals from the Era mine and Komsheche deposit in Iran. Raman spectroscopy, X-ray diffraction (XRD) analysis, photoluminescence (PL) spectroscopy, and diffuse reflectance spectroscopy were used to investigate the samples. The Raman spectra exhibited a distinctive peak at approximately  $322 \text{ cm}^{-1}$ , corresponding to the CaF<sub>2</sub> lattice vibration. XRD patterns confirmed the cubic phase of CaF<sub>2</sub>, and the preferred orientation of the (111) crystallographic plane was observed. The study revealed variations in full-width at half-maximum (FWHM) values among the samples, potentially indicating the presence of yttrium and enabling differentiation of Various fluorites from different regions. The results provide valuable insights into the structural and optical properties of fluorite crystals and contribute to the understanding of their formation and potential applications in various fields.

Keywords: Fluorite; Raman; XRD; PL; DRS

## Introduction

Fluorine compounds play a crucial role in various chemical and manufacturing procedures. Fluorspar, also known as a trade name of fluorite, is the primary fluorine mineral that is extensively mined. Fluorite is utilized directly as a material for fluxing and as an additive in diverse manufacturing processes. It serves as the primary source of fluorine in the creation of hydrogen fluoride or hydrofluoric acid, which is utilized as the raw material for numerous organic and inorganic chemical compounds. Fluorine plays a vital role in numerous industries, serving as an essential element in steelmaking, aluminum production, glass manufacturing, gasoline refining, and the production of enamels, insulating foams, refrigerants, and uranium for nuclear power [1]. Fluorite exhibits a chemical composition consisting of 51.2% calcium (Ca) and 48.8% fluorine (F). In some instances, it may contain chlorine (Cl), particularly in yellow varieties, as an isomorphous impurity or bituminous substances with a distinctive odor. Other impurities that may be present include iron oxide (Fe2O3), rare earth elements, and, on rare occasions, uranium, additional fluorine, and helium [2]. Fluorite, also known as CaF<sub>2</sub>, commonly contains impurities of Y in its crystalline structure. The  $Ca^{2+}$  ions are arranged in a cubic coordination with F<sup>-</sup> ions. The positioning of  $Ca^{2+}$  ions is such that they are distributed at both the corners and face centers within a cubic unit cell. On the other hand,  $F^-$  ions are located at the centers of the eight smaller cubes resulting from the division of the unit cell. Each Ca<sup>2+</sup> ion is connected to eight F<sup>-</sup> ions situated at the corners of a cube, forming a coordination arrangement. Specifically, the Ca<sup>2+</sup> ions envelop the F<sup>-</sup> ions at the corners, creating a tetrahedral configuration, as depicted in Figure. 1. The system itself is cubic, resulting in crystal formations that can take the shape of cubes, octahedrons, cubic octahedrons, and occasionally rhomb dodecahedrons. At times, the crystals can form visually appealing druses. Fluorite can be found in massive and veined forms, appearing as spherulites or rhythmically banded spherulite aggregates. The mineral is predominantly colorless or white, but can also exhibit shades of purple and green. Occasionally, polychromatic zonal crystals can be discovered. Fluorite possesses perfect cleavage parallel to the octahedron [111]. It has a glassy lustre, a hardness of 4, and a density of 3.18 gr/t. Notably, fluorite exhibits a purple or blue luminescence. Fluorite is commonly found in hydrothermal mineral deposits, often coexisting with sulfides like galena, sphalerite, and/or pyrite. Additionally, it forms associations with minerals such as calcite, dolomite, gypsum, barite, and quartz. In granites and pegmatites, fluorite emerges as a late-stage crystallization product. Geodes may also contain deposits of fluorite [3,4]. Fluorite is easily identified due to its chemical and physical properties that enhance its vivid color and fluorescence. In geological fields, fluorite plays an important role in the concentration and precipitation of rare metals. Consequently, it is often found in association with rich deposits of these valuable elements. In addition, fluorite tends to exhibit trace element compositions that reflect the formation fluid chemistry prevalent under diverse mineralization conditions. This feature suggests that fluorite compositions associated with specific deposit types have unique signatures. Consequently, fluorite has the potential to become a valuable tracer or geochemical indicator mineral [5]. Iran has a significant abundance of fluorite resources, with more than 30 known deposits and estimated reserves of more than 500,000 tons, with a base reserve of about 1 million tons. Currently, mining activities are concentrated in four key locations across different provinces. The largest reserves of fluorite in Iran are located in Mazandaran province with 83,000 tons, followed by Khorasan province with a significant reserve of 326,000 tons. Also, Isfahan province has reserves of 120,000 tons and Kurdistan province has 5,000 tons of fluorite reserves [6]. This paper considers four natural fluorite crystals from the Era mine and Komsheche deposit which are located in the Mazandaran and Isfahan regions, respectively. Mazandaran Fluorspar Mining District (MFMD) is located in the east of central Alborz mountains in northern Iran. Geographically, fluorite mineralization in the MFMD is classified into three main areas:

1. Swadkoh region including Pachi Miana, Shesh Rudbar, Baijan, Drasleh, and Ashjal mines.

- 2. Khatirkoh region, which includes Kammarpesht, Sarchalshak, Shurchal, Shoorakchal, and Kharch mines.
- 3. Kiasar region, Era, and Alikola mines.

The fluorite deposits in the MFMD are classified as Mississippi Valley fluorite-rich (MVT) deposits, and their host rock is known as Middle Triassic dolomite. Mineralization in these deposits includes a variety of minerals such as fluorite, barite, galena, calcite, pyrite and, dolomite [7-14]. The Komsheche deposit is located in the Middle Triassic dolomite of Central Iran in the Isfahan region. The type of ore deposit is MVT and the most important mineralization consists of Barite, Fluorite, Galena, Calcite, and Quartz [15-16]. The samples have been subjected to a comprehensive study to determine a method to evaluate their structural and optical characteristics. In this work, we compare the information obtained by Raman, photoluminescence and reflectance spectroscopy, and XRD diffraction studies.



Figure 1: A view of the crystal structure of fluorite (Adapted from Klein & Philpotts, 2013).

## Experimental

#### Materials

This research was carried out on fluorite from two different areas in Iran. Figure. 2 shows three fluorite samples related to the Alborz region, Era fluorite mine (E, EB, FB), and one fluorite sample related to the Central Iran region, Komshecheh deposit (G). These samples have been investigated by Raman, Photoluminescence, diffused reflectance spectroscopy, and XRD analysis



Figure 2: Photos of E, EB, FB and G samples.

#### Methods

The investigation of all samples was conducted using a Micro Raman Spectroscope (532i Avantes). For each sample, three measurements were performed at distinct points. The diffraction peak intensity of the fluorite samples was normalized using Origin 2018 software. The X-ray diffraction (XRD) analysis was carried out using the AW-XDM300 instrument. This instrument is equipped with a CuK $\alpha$  radiation source with a wavelength of 1.54184 Å. The XRD data were collected with a step size of 0.05° 2 $\theta$ , and each step had a counting time of 1 second. The photoluminescence emission (PL) spectra were tested by Shimadzu RF-600 fluorescence spectrometer. Diffuse Reflectance Spectroscopy (DRS) was tested using a UV-3600 spectrophotometer produced by Shimadzu, Japan. DRS measurements were recorded from 300 to 1800 nm.

## **Results and discussion**

#### Raman spectroscopy

The Micro-Raman spectra of the samples, utilizing a 532 nm excitation, are presented in Figure. 3. In this figure, a distinctive Raman peak is consistently observed for all samples from different areas, appearing at approximately 322 cm<sup>-1</sup> [17]. This observation aligns with the fluorite peak documented in the RRUFF database (ID: R050046). Studies by Tsuda et al. [18] elucidated that this Raman signal corresponds to the CaF2 lattice vibration at 322 cm<sup>-1</sup>. Russell [19] obtained Raman peak of fluorite at 322 cm-1. Additionally, Liu et al. [20] reported a Raman peak at 320 cm-1 for white fluorite. Lewandowski et al. [21] observed Raman peak at 319.13 cm-1 for calcium fluoride. This specific peak at around 320-322 cm<sup>-1</sup> is attributed to the T2g Raman active vibrational mode of fluorite [17], [22-26]. It's worth noting that white fluorite typically exhibits a single Raman peak at around 320 cm<sup>-1</sup>, while non-white fluorite may display additional peaks at different locations [19]. In all analyzed specimens, the Raman active T2g vibration mode of CaF2 was observed. The observed frequency shift and full-width at half-maximum (FWHM) broadening of this mode are indicative of defects and impurities within the CaF2 lattice [27]. additionally, the broadening of the full width at half maximum (FWHM) in Raman spectra due to the presence of yttrium (Y) in fluorite can be attributed to its impact on the crystal lattice. Specifically, when Y+3 ions substitute for Ca+2 in the CaF2 lattice, they introduce substitutional defects due to the difference in ionic radii (Y+3  $\approx$  0.90 Å vs. Ca+2  $\approx$  1.00 Å) and charge imbalance. This substitution leads to local lattice distortion and strain, as well as the need for charge compensation mechanisms (e.g., formation of vacancies or interstitial defects). indicating that higher Y content contributes to greater lattice disorder and thus broader Raman peaks [28]. The FWHM values for the samples E, EB, FB, and G are distinct, measuring 18.29, 17.67, 19.19, and 19.06, respectively, as indicated in Table 1. FWHM is a critical parameter that can be used to differentiate fluorites originating from different regions.



Figure 3: Raman spectra of fluorites from Alborz (E, EB, FB) and Central Iran (G) regions in Iran.

Sample	Peak position(2θ)	FWHM	Crystallite size (nm)	Raman Shift (cm <sup>-1</sup> )	FWHM(cm <sup>-1</sup> )	Y(ppm)
E	28.26	0.12	67.6	322	18.29	1.5
EB	28.26	0.12	66.1	322	17.67	0.6
FB	28.26	0.11	73.2	322	19.19	3.4
G	28.26	0.13	59.8	322	19.06	2

Table 1: The structural parameters of the four fluorite samples.

### **XRD** analysis

Figure. 4 displays the X-ray diffraction (XRD) patterns for all investigated samples. The diffraction peaks observed in the patterns can be accurately identified as (111), (220), (311), (400), (331), and (422) of the cubic phase of CaF2, characterized by the Fm3m (225) space group [29-31]. These findings are in agreement with the standard values determined for cubic CaF2 (ICSD No. 00-035-0816). we utilized Origin 2015 software to normalize the diffraction peak intensity of the fluorite samples. XRD results of fluorites indicate that the preferred orientation (111) for E, EB, FB, and G samples was observed at  $2\theta = 28.26^{\circ}$ . Similarly, Wang et al. [30] showed the (1 1 1) crystallographic plane as the preferred orientation of CaF2. To study the fluorites from different regions, various parameters including peak position, the crystallite size (D) and, FWHM were measured and are detailed in Table 1. The crystallite size for all samples was calculated using the Debye-Scherrer formula [32-33].

$$D = \frac{k\lambda}{\beta\cos\theta}$$

where  $\beta$  is the FWHM,  $\lambda$  is the wavelength of the X-ray (1.5418 Å), K is the Scherrer constant (usually K = 0.9) dependent on the crystallite shape and  $\theta$  is the Bragg angle at the center of the peak.

Table 1 provides the results obtained from the analysis of the X-ray data for different samples. Notably, the FWHM of the preferred orientation peak for samples E, EB, FB, and G is recorded as 0.12, 0.12, 0.11, and 0.13, respectively Additionally, the crystallite size for different samples was calculated using the dominant (111) peak, resulting in sizes of 67.6, 66.1, 73.2, and 59.8 nm, respectively. Il'ves et al. [34] calculated the FWHM of the diffraction peak of initial and annealed CaF2 samples and obtained values of 0.141, 0.22 and, 0.101 for them. The study conducted by Zahedifar et al. [35] reported the crystallite size of CaF2 using the dominant (220) peak, and the calculated value was approximately 43 nm.



Figure 4: XRD patterns of four fluorites from different regions

## **ICP** analysis

The Yttrium (Y) content in fluorites was determined through Inductively Coupled Plasma (ICP) analysis. According to Table 2, the highest Yttrium concentration is observed in the FB sample, with a value of 3.4 ppm, while the lowest concentration is found in the EB sample, at 0.6 ppm. The amount of yttrium in the E sample is 1.5 ppm and in the G sample is 2 ppm (Table 2). The comparison of Yttrium (Y) element values in different fluorites with FWHM values in Raman analysis revealed a direct relationship between FWHM and increasing Y values. Specifically, sample FB, with the highest Y value of 3.4 ppm, exhibited the highest FWHM. Conversely, sample EB, with the lowest Y value of 0.6 ppm, demonstrated the lowest FWHM [27].

**Table 2:** The average Yttrium values of the samples.

Sample	Е	EB	FB	G
Y(ppm)	1.5	0.6	3.4	2

#### Photoluminescence Spectroscopy

The simultaneous determination of the emission wavelength (Em) range and excitation wavelength (Ex) range for the samples can be achieved by measuring the 3D spectrum within the ranges of 400 to 600 nm for emission and 330 to 390 nm for excitation, respectively. In the representation of the 3D spectrum, the y-axis corresponds to the Ex, while the x-axis represents the fluorescence wavelength (Em) (Figure. 5). The color red is indicative of areas with strong fluorescence, whereas blue represents weaker fluorescence areas [36]. The analysis based on Figure. 5 involved the reduction of 3D images of photoluminescence (PL) in the emission range of 400 to 440 nm for samples E, EB, FB, and G, respectively. To validate this observation, the emission values of the samples were specifically investigated at 420 nm for an excitation wavelength of 350 nm, as shown in Table 3. The study of the PL spectra of fluorite at excitation wavelengths of 260 nm aimed to investigate the factors contributing to the variation in PL emission (Figure. 6). Under the excitation of 260 nm, the PL emission peaks of samples E, EB, FB, and G are observed at 364 and 510 nm. Consequently, the PL emission peak of fluorites from different areas under a short wave is mainly at 510 nm, and the intensity is weak [20]. The presence of the Yttrium (Y) element is considered one of the reasons why fluorite exhibits fluorescence [20], [37-41]. According to Table 2, the concentrations of Y in samples E, EB, FB, and G are recorded as 1.5, 0.6, 3.4, and 2 ppm, respectively. The study conducted by Liu et al. [20] involved an investigation of the photoluminescence (PL) spectra of fluorite at excitation wavelengths of 365 and 254 nm. The primary objective was to understand the factors con-

tributing to the variation in PL emission. The study conducted by Il'ves et al. [34] investigated the photoluminescence (PL) of CaF2 samples, revealing broad bands with maxima at a wavelength of approximately  $\lambda max \sim 684$  nm. The observation that the amount of fluorescence in the Alborz region samples (E, EB, FB) appears to be higher than in the Central Iran region sample (G) suggests a potential distinguishing characteristic between fluorites from these different regions.



 Table 3: Photoluminescence value of the samples at excitation 350 nm, Em 420nm.



Figure 5: 3D florescence Spectrum mode of the four fluorite samples.



**Figure 6:** Emission spectrum of samples at  $\lambda$ EX= 260 nm

#### Diffuse Reflectance Spectroscopy

The principle of diffuse reflectance spectroscopy is to measure the absorption of electromagnetic radiation within the wavelength range of 300 nm to 1800 nm. This absorption is caused by the vibrations of the molecular bonds in minerals, which include rotation, bending, and stretching motions, as they interact with the incident electromagnetic radiation. Various parameters, such as structure, cation size, charge, and electronegativity, determine the shape and precise position of the characteristic absorption bands for each mineral. These absorption bands offer valuable insights into the mineral's specific structure and composition [42]. Based on Figure. 7, it is observed that in the ultraviolet range (300-400 nm), the samples E, EB, G, and FB exhibit the highest reflection intensity in that order. In the visible range (400-800 nm), as the wavelength increases, the highest reflectance is observed in the samples EB, G, E, and FB in that order. Similarly, in the infrared range, the samples EB, G, E, and FB show the highest intensity of reflection, respectively. The differences observed in the DRS Spectrum of the fluorite samples suggest variations in crystal composition, particularly in trace element content and structural defects. Considering that the FB sample, which exhibited the lowest reflectance in the UV, visible, and IR ranges, also contained the highest concentration of yt-trium (3.4 ppm), in ICP results. This reduction in reflectance intensity can be attributed to increased lattice disorder and the presence of substitutional impurities, such as Y+3 replacing Ca+2. These substitutions lead to the formation of defect states within the band gap. Such defects can absorb more incident light or scatter it non-uniformly, thereby decreasing the overall reflectance. The fluorite mineral has a large bandgap, which is located in the high-ultraviolet region at around 10 eV [43]. As a result, the absorption edge of fluorite occurs at 100 nm, leading to a high reflectance in the near-UV region (200 nm). Consequently, it becomes difficult to determine the precise band gap value. Aimacaña et al. [44] conducted Diffuse Reflectance UV-Vis spectroscopy on part-CaF2 powder to analyze its optical characteristics. Ge et al. [17] examined the UV-visible spectra of three fluorite samples with different colors.



Figure 7: Diffuse reflectance spectrum of the four fluorite samples.

## Conclusions

In this study, the structural and optical properties of four fluorite samples from the Alborz and Central Iran regions in Iran were investigated. The Raman investigations indicated that the samples exhibited the same Raman shift; however, the presence of the Yttrium element resulted in different FWHM values. The XRD analysis revealed distinct crystal properties (crystallite size) for the fluorites from these two regions. Furthermore, 3D images of photoluminescence in the emission range of 400 to 440 nm displayed varying and decreasing emission values for the samples. The optical properties, as determined by reflectance measurements, showed that the reflection intensity of the samples differed and changed in the ultraviolet, visible, and infrared ranges.

## References

1. TS Hayes, MM Miller, GJ.Orris, NM Piatak, Fluorine, (2017) Chapter G of Critical Mineral Resources of the United States Economic and Environmental Geology and Prospects for Future Supply.

2. Betekhtin (1966) A course of mineralogy.

3. AV Milovsky, OV Kononov (1985) Mineralogy, Mir publishers Moscow.

4. C Klein, AR Philpotts, (2013) Earth Materials: Introduction to mineralogy and petrology.

5. S Makin (2013) Developing fluorite as a geochemical pathfinder mineral using globally reported REE- Y contents. B.Sc., Stockton University.

6. M Ghorbani (2013) The Economic Geology of Iran: Mineral Deposits and Natural Resources 1-450.

7. B Shafiei Bafti, I Dunkl, S Madanipour (2021) Geological Magazine.

8. S Zabihitabar, B Shafiei, H Mirnejad (2017) J. Geol. 9: 75-92.

9. G Vahab-zadeh, A Khakzad, I Rasae, M R Mousavi (2008) Journal of Sciences, 18, 99108.

10. F Nabiloo, B Shafiei Bafti, A Amini, (2017) J. Econ. Geol. 9, 483-507.

11. S Alirezaei (1985) An investigation in stratigraphy and genesis of F-Pb-Ba deposits in the Central Alborz. M.S. thesis. Tehran University, Iran (in Persian).

12. Z Mehraban (2016) Geochemistary of REEs in the fluorite (±Pb, Ba) mine of Savadkuh region, Mazandaran province. M.S. thesis. Golestan University (93 pp in Persian).

13. M Lotfi, M Hekmatian, AA Shabani, M Mokhtari (2015) Sci. Quart. J. Geosci, 24: 73-84.

14. AR Rajabi, E Rastad, C Canet (2013) Australian Journal of Earth sciences 60: 197-216.

15. Z Alaminia, M Tadayon, EM Griffith (2021) Chemical Geology 566: 120084.

16. M.A. Rajabzadeh (2007) Iran. J. Sci. Technology 31: 73-87.

- 17. X Ge, Q Guo, Q Wang, T Li, L Liao (2022) Materials 15: 1983.
- 18. H Tsuda, WL Jongebloed, I Stokroos, J Arends, Caries Res (1993) 27: 445-54.
- 19. S Ganesan, E Burstein, Journal de Physique, (1965) 26: 645-8.
- 20. Y Liu, Q Guo, L Liu, S Zhang, Q Li, L Liao, Crystals, 2023, 13, 75.
- 21. B Lewandowskia, BB Saida, M Ulbrichtb, G Krekela (2019) Minerals Engineering 135: 129-38.
- 22. VG Keramidas, WB White (1973) J. Chem. Phys 59: 1561-2.
- 23. R Srivastava, HV Lauer, LL Chase, WE Bron Phys. Lett A (1971) 36: 333-4.

24. I Alencar, J Ruiz-Fuertes, K Schwartz, C Trautmann, L Bayarjargal, E Haussühl, B Winkler, J Raman Spectrosc (2016) 47: 978–83.

25. ZC<sup>\*</sup> ermáková, P Bezdic<sup>\*</sup>ka, I Ne<sup>\*</sup>mec, J Hradilová, V Šrein, J Blažek, D Hradil (2015) Acta Crystallogr. Sect. A Found. Adv

#### 71: s529-30.

- 26. M Mujaji, JD Comins (2007) phys. stat. sol. (c) 4: 851-5.
- 27. L Su, J Xu, W Yang, X Jiang, Y Dong (2005) Chin. Opt. Lett 3: 219-21.

28. Shannon RD (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Foundations of Crystallography 32: 751-67.

29. The assignments of product phase were based on the Joint Committee for Powder Diffraction Studies (JCPDS) database—International Center for Diffraction Data, PCPDFWIN v.2.02. JCPDS File No. 35–081622, 1999.

- 30. H Wang, R Liu, K Chen, X Shi, Z Xu (2011) Thin Solid Films 519: 6438-42.
- 31. K Tahvildari, M Esmaeili pour, Sh Ghammamy, H Nabipour (2012) Int.J.Nano Dim 2: 269-73.
- 32. BE Warren (1990) X-ray Diffraction.
- 33. MM Shahidi, MH Ehsani, H Rezagholipour Dizaji, ME Ghazi (2020) J Mater Sci: Mater Electron 31: 2030-39.
- 34. VG Il'ves, SY Sokovnin, MG Zuev (2019) Phys. Solid State 61: 2200-17.
- 35. M Zahedifar, E Sadeghi, S Harooni (2012) Nuclear Instruments and Methods in Physics Research Section B 291: 65-72.
- 36. K Maruyama, K Sobue, SHIMADZU (2022) Excellence in science.
- 37. M Gaft, GA Waychunas, GR Rossman, L Nagli, Y Raichlin (2020) Phys.Chem.Miner 47: 46.
- 38. A Sidike, I Kusachi, N Yamashita (2003) Phys. Chem. Miner 30: 478-85.
- 39. M Pagel, V Barbin, P Blanc, D Ohnenstetter (2000) Springer: Berlin/Heidelberg, Germany 127-60.
- 40. S Ye, B Zhu, J Chen, J Luo, JR Qiu (2008) Appl. Phys 92: 34-6.
- 41. DR Tallant, JC Wright (1975) J. Chem. Phys 63: 2074-85.
- 42. C Arbiol, GD Layne (2021) Appl Spectrosc 75: 1475-96.
- 43. RA Heaton, CC Lin (1980) Phys. Rev.B 22: 3629-38.

44. CMC Aimacaña, KO Pila, DA Quinchiguango Perez, A Debut, MF Attia, R Santos-Oliveira, DC Whitehead, C Reinoso, F Alexis (2021) Molecules 26: 5447.