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Chemical Composition and Spectroscopic Characteristics of Alexandrite Effect Apatite from the Akzhailyau Mountains of Kazakhstan

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Abstract: The alexandrite effect is a pivotal optical phenomenon in gemmology, evident in several notable gemstones. However, the manifestation of this effect in apatite from Kazakhstan stands out as both rare and highly sought after. This apatite displays a yellowish-green hue in daylight and transitions to a pinkish-orange shade under incandescent lighting. This research involved analyzing the apatite's chemical composition using LA-ICP-MS, in addition to obtaining its infrared, Raman, UV-Vis, and fluorescence spectra. From the elemental assessment results, the primary trace elements in the apatite were identified as Na, Mn, and Fe, along with rare-earth elements including Gd, Dy, Ce, Nd, and Sm. The infrared and Raman spectra showcased peaks corresponding to phosphate and hydroxyl groups. The apatite's alexandrite effect predominantly stems from absorption peaks at 748, 738, 583, 578, and 526 nm in the visible spectrum, all of which are attributed to the rare-earth element, Nd. The fluorescence peaks of the apatite are primarily influenced by elements such as Ce, Eu, Nd, and Mn. Through this research, a theoretical foundation has been laid for the non-destructive identification of apatite exhibiting the alexandrite effect.

Keywords: apatite; alexandrite effect; Raman and infrared spectroscopies; UV-Vis and fluorescence spectroscopies; chemical composition



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1. Introduction

Apatite is a phosphorus mineral characterized by a complex chemical composition. Its general formula is $A_{10}[PO_4]_6Z_2$ [1–9]. In this formula, 'A' signifies a divalent cation, primarily represented by Ca^{2+} . However, it can also be Mg^{2+} , Fe^{2+} , Sr^{2+} , Mn^{2+} , Pb^{2+} , and Cd^{2+} , among others [1–3]. Rare-earth element ions, such as Ce^{3+} , Nd^{3+} , La^{3+} , and Sm^{3+} , as well as alkali metal ions, such as Na^+ and K^+ , can occupy the 'A' site through isomorphic substitutions [1–3]. Within the crystal structure, there are two coordination positions for the A ions: Ca1, with a coordination number of 9, and Ca2, with a coordination number of 7. The ratio of Ca1 to Ca2 in the unit cell is 4:6 [1–3]. Furthermore, $[PO_4]^{3-}$ can be replaced by $[SiO_4]^{4-}$, $[SO_4]^{2-}$, or especially $[CO_3]^{2-}$ [1–3]. The 'Z' site can host ions such as F[−], OH[−], or Cl[−] [1–3]. When used as a gemstone, apatite is typically known as fluorapatite. According to [9], its basic chemical formula showcasing the alexandrite effect is $Ca_{10}[PO_4]_6F_2$. In this configuration, some of the Ca is substituted by elements such as Mn, Ce, Nd, La, and Sm. Additionally, portions of $[PO_4]$ are replaced by $[SiO_4]$, and some F ions are substituted by OH [4–8]. These variations manifest as different shades of apatite—blue, yellow, pink, and green—which enhance its appeal in the gemstone market [4–8]. In gemological terms, the frequent isomorphic substitutions in apatite lead to diverse defects, presenting as different colors [4–8]. Ideally, as an allochromatic gemstone, clear apatite should be colorless. However, its proclivity for isomorphous substitutions and crystal structure changes render it multicolored. These vibrant hues can be largely attributed to

the presence of rare-earth elements (REE), transition metal ions (primarily Mn and Fe), and, more broadly, color centers [4–8].

It is well established that the most sought-after apatite boasts a bluish-green hue, reminiscent of Paraiba tourmaline. Consequently, green fruits might be treated to attain a blue or bluish-green shade to enhance their value [6]. Another variety of apatite, which exhibits the color-changing phenomenon termed the alexandrite effect, also holds significant value [9]. This alexandrite effect is discernible in various gemstones, including alexandrite, sapphire, garnet, and spinel [10]. Earlier in this century, large apatite crystals that change color under different light sources were discovered in the Akzhailyau Mountains of Kazakhstan. These mountains are situated in the Semipalatinsk region of eastern Kazakhstan, near the Chinese border, and form the northwestern segment of the Tarbagatai Mountain range. Geologically, the Akzhailyau Mountains comprise Akzhailyau granites, along with neighboring metamorphic and effusive sedimentary rocks from the Silurian, Devonian, and Carboniferous periods. These rocks undergo significant alteration upon contact with the granites. The Akzhailyau pegmatites teem with a plethora of minerals. Notably, these minerals—ranging from feldspar, quartz, and apatite to mica, rare metal minerals, tourmaline, and fluor spar—are almost perfectly crystallized. In this milieu, the Akzhailyau apatite stands out as a quintessential pegmatite mineral. The apatite crystals are typically hexagonal, favoring a long prismatic shape over a short one. They range from transparent to translucent with well-defined facets. Depending on the rough stone's quality, it is feasible to craft faceted gemstones ranging from 0.5 to 15 carats. Notably, under incandescent light, the apatite crystals exude a pinkish-orange hue, which transforms into a greenish-yellow in daylight [9].

Currently, non-destructive spectroscopic techniques are pivotal in gemological research. These techniques can furnish crucial insights for the non-destructive identification of gemstones [11–27]. Among the array of non-destructive spectroscopic methods employed to study gemstones, the most prevalent are infrared spectroscopy, Raman spectroscopy, ultraviolet–visible spectroscopy, and fluorescence spectroscopy [11]. Both infrared and Raman spectroscopy have carved a niche in archaeological endeavors linked to gemology [13–20]. For instance, they facilitate the swift, non-invasive identification of gemstones and minerals present in artifacts [13,15,17,18]. The utilization of non-destructive spectroscopy in this interdisciplinary domain is witnessing a surge [19]. Apatite exhibiting a distinctive alexandrite effect is a rarity that captivates gemologists and mineralogists. Nonetheless, gemological studies on this type of apatite are sparse. To address this, we amassed vibrational spectra (infrared and Raman) and electronic spectra (UV-Vis and fluorescence) of this apatite. Concurrently, we evaluated its trace element composition via laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Our comprehensive analysis shed light on the chemical composition and spectroscopic attributes of this apatite, thereby laying a foundational framework for the non-invasive identification of apatite affected by the alexandrite phenomenon.

2. Materials and Methods

2.1. Materials

The experimental sample consisted of a rough apatite stone sourced from Kazakhstan. As depicted in Figure 1, the crystals from the stone are well-developed and prominently display the alexandrite effect. To ensure experimental precision and mitigate any impact of surface irregularities on the results, two slices were sectioned from the stone in distinct orientations—one parallel and the other perpendicular to the *c*-axis. The slice cut perpendicular to the *c*-axis was labeled as slice-1, while the one cut parallel to the *c*-axis was designated as slice-2. These slices were then polished to the thicknesses of 0.183 cm and 0.165 cm, respectively. Subsequently, the surface of each slice was cleaned with alcohol and allowed to dry before further characterization.



Figure 1. Alexandrite effect apatite sample (the top shows samples under daylight and the bottom shows samples under incandescent).

2.2. Methods

The LA-ICP-MS analysis was conducted at Wuhan SampleSolution Analytical Technology Co., Ltd. The GeolasPro laser ablation system utilized included a COMPexPro 102 ArF 193 nm laser coupled with a MiroLas optical system. The study employed an Agilent 7900 ICP-MS instrument. Parameters set included a laser spot diameter of 44 μm , a laser frequency of 5 Hz, and an energy density of 5.5 J/cm². The chosen glass reference materials encompassed BHVO-2G, BCR-2G, BIR-1G, and NIST 610. The acquired data was subsequently analyzed using a multi-external standard, with no internal standard method, aided by the software ICPMSDataCal (version11.8) [28].

At the Gemmological Institute of the China University of Geosciences (Wuhan), infrared, Raman, UV-Vis, and fluorescence spectra were captured. The Raman spectra were recorded using a Jasco NRS-7500 Raman spectrometer with the set conditions as follows: range 400–1600 cm^{−1}, exposure time of 20 s, accumulation of 5 times, a 633 nm laser wavelength, and 2 mW laser power. The infrared spectra were derived from a Bruker HYPERION 3000 + Fourier transform infrared spectrometer, operating in transmission and reflection modes, at a rate of 4 cm^{−1} over 64 scans. The signal was acquired in the range of 400–4000 cm^{−1}. The UV-Vis spectra were acquired with a PerkinElmer Lambda 650S UV-Vis spectrophotometer in transmission mode, covering a range of 400–780 nm, a 1 nm data interval, and scanning at a rate of 267 nm/min. The fluorescence spectra were recorded using a Jasco FP8500 fluorescence spectrometer. The conditions included an excitation light source with a wavelength range of 200–728 nm, a bandwidth of 5 nm, and a data interval of 2 nm; a fluorescence collection range of 220–750 nm, a bandwidth of 2.5 nm, and a data interval of 1 nm; a detector scan speed of 1000 nm/min; and a detector voltage set to 390 V. All analyses were performed at a controlled room temperature of 25 °C.

3. Results and Discussion

3.1. Chemical Composition Characteristics of Alexandrite Effect Apatite

Apatite has a notable concentration of transition and rare-earth elements, which can influence its spectroscopic characteristics and the alexandrite effect [8]. Hence, to delve deeper into the gemological properties of apatite, comprehending its chemical composition is pivotal. The elemental content for the two slices is detailed in Table 1 and illustrated in Figure 2. Rare-earth elements (REEs), sharing closely related chemical properties, are typically split into two primary categories based on their double-salt solubility: the light rare-earth elements (LREEs), which comprise the cerium subgroup elements (spanning from lanthanum to europium), and the heavy rare-earth elements (HREEs), encompassing the yttrium subgroup elements (from gadolinium to lutetium, including yttrium) [29,30]. In the samples, the earth elements are bifurcated into light and heavy rare-earth categories, as

depicted in Figure 2. It is noteworthy that Yttrium (Y) is categorized as a heavy rare-earth element, and given its substantial presence, its content is reserved for the rightmost column of Table 1. For clarity in presentation, Yttrium is excluded from Figure 2.

Table 1. Element content of alexandrite effect apatite (wt%).

	CaO	P ₂ O ₅	Na ₂ O	MnO	FeO	Y
slice-1	56.72	42.44	0.02527	0.09596	0.01459	0.1896
slice-2	56.41	42.63	0.03295	0.1038	0.01573	0.2486

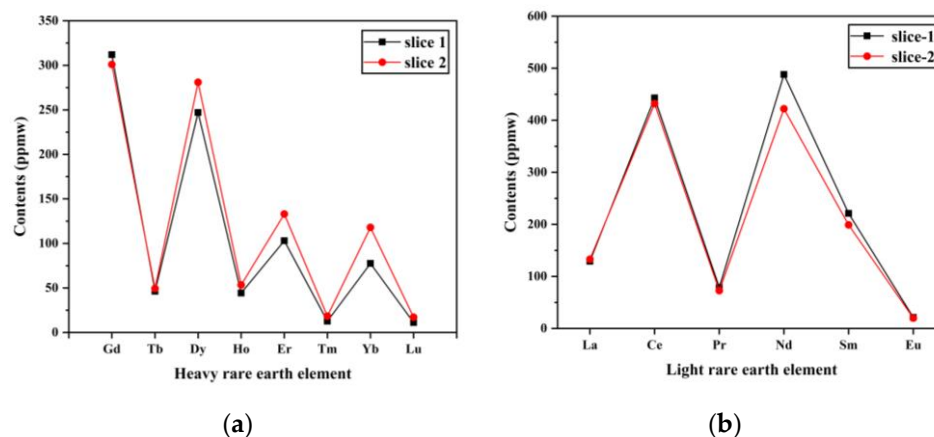


Figure 2. (a) Heavy rare-earth element content of alexandrite effect apatite. (b) Light rare-earth element content of alexandrite effect apatite.

It can be observed from Table 1 and Figure 2 that, in addition to Ca and P, this apatite contains transition elements, including Mn, Fe, and rare-earth elements. In natural apatite, light rare-earth elements mainly occupy Ca2 sites in the lattice, whereas heavy rare-earth elements prefer to occupy Ca1 sites [2,30]. The light rare-earth elements were La, Ce, Pr, Nd, Sm, and Eu, and the heavy rare-earth elements were Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y. Light rare-earth elements, such as Ce and Nd, are abundant in these apatite samples. Furthermore, Y, Gd, and Dy contents of the heavy rare-earth elements were relatively high.

3.2. Vibrational Spectral Characteristics of Alexandrite Effect Apatite

Raman and infrared spectroscopies are two of the most commonly used vibrational spectroscopic techniques in gemological research [31–40]. Simultaneously, these two spectroscopic techniques are important tools for the examination of apatite mineral species and composition and exhibit a wide range of applications to obtain more comprehensive mineralogical information with respect to apatite.

3.2.1. Raman Spectra of Alexandrite Effect Apatite

The Raman spectra of slice-1 and slice-2 are shown in Figure 3a,b, respectively. Peaks were observed at 1084, 1060, 1035, 965, 606, 580, and 448 cm^{−1} in the Raman spectrum of slice-1. Furthermore, peaks at 1083, 1053, 965, 606, 591, 452, and 430 cm^{−1} were observed in the Raman spectrum of slice-2. It can be observed that the Raman spectra of these two slices differ to an extent because they were cut in different crystal orientations. However, the characteristics of [PO₄]^{3−} are similar. The phosphate of apatite has four vibration modes: symmetric stretching vibration peak (ν₁), located at about 965 cm^{−1}; bending vibration peak (ν₂), located at about 419–440 cm^{−1}; asymmetric stretching vibration peak (ν₃), located at about 1040–1049 cm^{−1}; and asymmetric bending vibration peak (ν₄), located at approximately 575–593 cm^{−1} [35–40]. The Raman peaks of the two slices and their assignments are listed in Table 2.

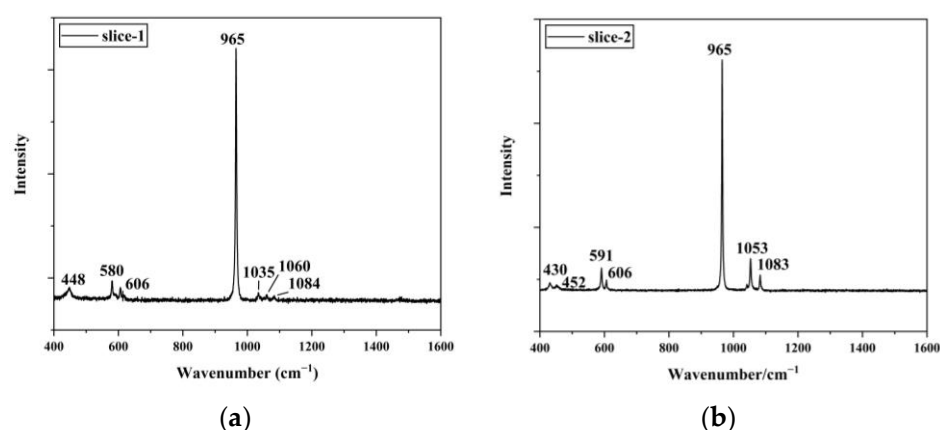


Figure 3. (a) Raman spectrum of slice-1 and (b) Raman spectrum of slice-2.

Table 2. Raman peaks of alexandrite effect apatite and the assignments of these peaks.

Assignments	Raman Peaks of Slice-1/cm ⁻¹	Raman Peaks of Slice-2/cm ⁻¹
ν_1 (symmetric stretching of $[\text{PO}_4]^{3-}$)	965	965
ν_2 (bending of $[\text{PO}_4]^{3-}$)	448	452, 430
ν_3 (asymmetric stretching of $[\text{PO}_4]^{3-}$)	1084, 1060, 1035	1083, 1053
ν_4 (asymmetric bending of $[\text{PO}_4]^{3-}$)	606, 580	606, 591

In apatite crystals, $[\text{PO}_4]^{3-}$ can be substituted with other complex anions such as $[\text{CO}_3]^{2-}$. The presence of $[\text{CO}_3]^{2-}$ is shown in the Raman spectrum, mainly in the ν_1 mode located at 1070 cm^{-1} . However, it is often neglected because it overlaps with the ν_1 mode of $[\text{PO}_4]^{3-}$ ($1033\text{--}1080\text{ cm}^{-1}$). The Raman modes of ν_2 , ν_4 , and ν_1 of $[\text{CO}_3]^{2-}$ are not obvious. Furthermore, ν_3 mode in the range of $1410\text{--}1495\text{ cm}^{-1}$, ν_2 mode at 878 cm^{-1} , and ν_4 mode at $671\text{--}758\text{ cm}^{-1}$ can be determined to confirm their presence [16,19]. None of the peaks of $[\text{CO}_3]^{2-}$ were observed in the Raman spectra of the alexandrite effect apatite [16], indicating that $[\text{PO}_4]^{3-}$ was not replaced by $[\text{CO}_3]^{2-}$. Additionally, no peaks of complex anions other than $[\text{PO}_4]^{3-}$ were found in the Raman spectra.

3.2.2. Infrared Spectra of Alexandrite Effect Apatite

In the fingerprint region of the infrared spectrum of apatite, four main vibrations of phosphate are present: symmetric stretching vibration (ν_1), bending vibration (ν_2), asymmetric stretching vibration (ν_3), and bending vibration (ν_4) [38–40]. If the phosphate in apatite is replaced by other complex anions, then the position of the IR peak in the fingerprint region changes. Thus, the phosphate in apatite can also be observed via the fingerprint region of the infrared spectrum of apatite. If the structure of apatite contains hydroxyl groups, then the peaks of hydroxyl groups can be observed in the range of $3000\text{--}4000\text{ cm}^{-1}$ of the infrared spectrum [35]. Therefore, we show the infrared spectra in the range of $400\text{--}1300\text{ cm}^{-1}$ (reflection method) and infrared spectra in the range of $3000\text{--}4000\text{ cm}^{-1}$ (transmission method) of the alexandrite effect apatite (Figure 4) to observe the phosphate and hydroxyl groups in this apatite. It is well established in previous studies [12,15] that the orientation of the crystal can affect the spectral response in terms of the position and intensity of the bands in the infrared spectra. Therefore, it is essential to consider the infrared spectral characteristics of apatite in varying crystal orientations. Figure 4 displays the infrared spectra for slice-1 and slice-2, with the corresponding assignments for these spectral peaks provided in Table 3.

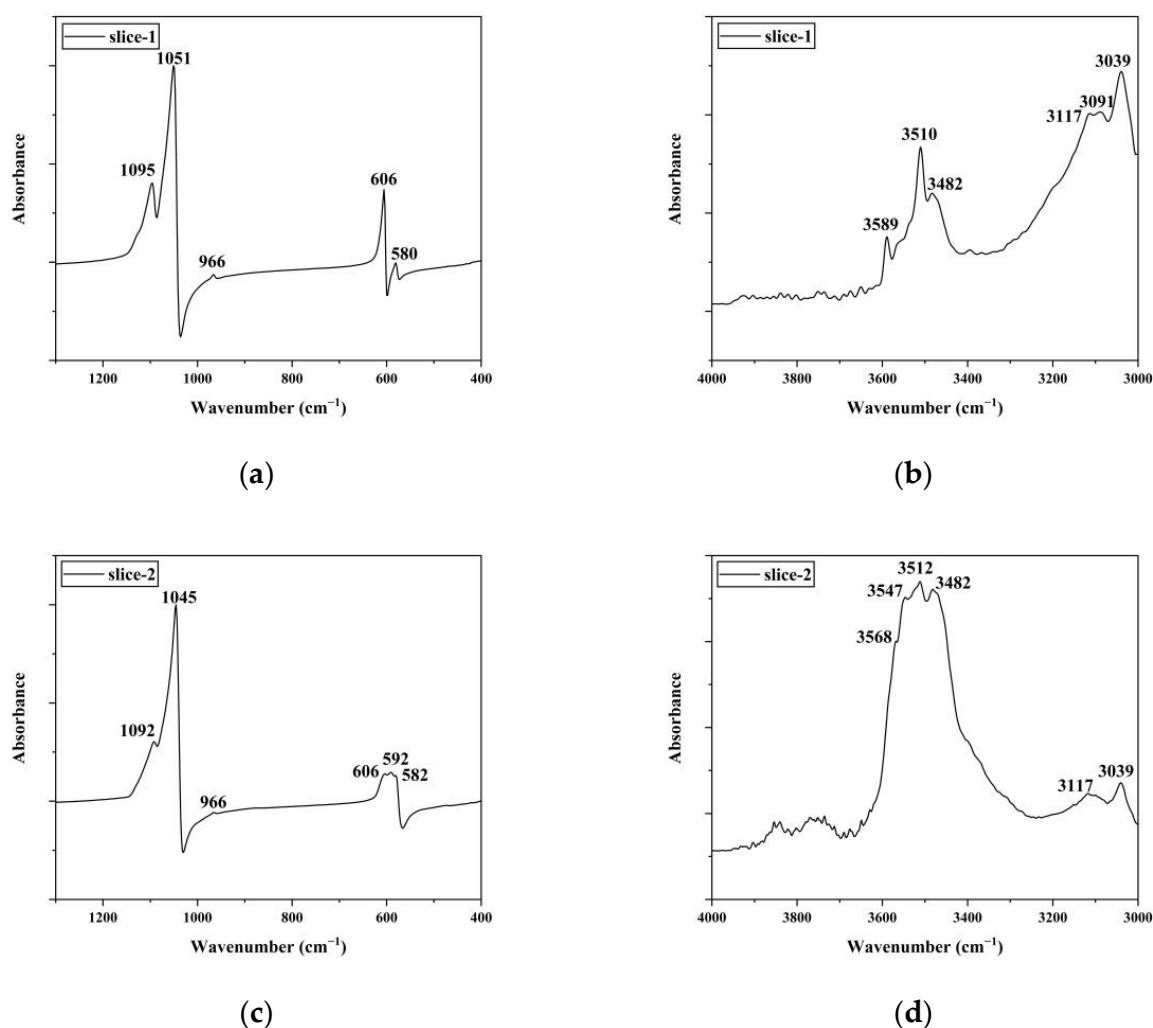


Figure 4. (a) Infrared spectrum of slice-1 (400–1300 cm^{-1}). (b) Infrared spectrum of AP-1 (3000–4000 cm^{-1}). (c) Infrared spectrum of slice-2 (400–1300 cm^{-1}). (d) Infrared spectrum of AP-2 (3000–4000 cm^{-1}).

Table 3. Infrared spectral peaks of alexandrite effect apatite and assignments of these peaks.

Assignments	Infrared Spectral Peaks of Slice-1/ cm^{-1}	Infrared Spectral Peaks of Slice-2/ cm^{-1}
ν_1 (symmetric stretching of $[\text{PO}_4]^{3-}$)	966	966
ν_3 (asymmetric stretching of $[\text{PO}_4]^{3-}$)	1095, 1051	1092, 1045
ν_4 (asymmetric bending of $[\text{PO}_4]^{3-}$)	606, 580	606, 592, 582
OH stretching	3589, 3510, 3482, 3117, 3091, 3039	3568, 3547, 3512, 3482, 3117, 3039

According to Figure 4, the infrared spectrum of slice-1 presents peaks at 1095, 1051, 966, 606, and 580 cm^{-1} in the 400–1300 cm^{-1} range, and peaks at 3589, 3510, 3482, 3117, 3091, and 3039 cm^{-1} in the 3000–4000 cm^{-1} range. Based on Figure 4c,d, the infrared spectrum of slice-2 exhibits peaks at 1092, 1045, 966, 606, 592, and 582 cm^{-1} in the 400–1300 cm^{-1} range, and peaks at 3568, 3547, 3512, 3482, 3117, and 3039 cm^{-1} in the 3000–4000 cm^{-1} range. Differences in the positions and intensities of the infrared peaks (attributed to phosphates and hydroxyls) arise from the distinct crystal orientations of the tested samples [15]. From Figure 4a,c, when the c -axis of the crystal aligns parallel to the incident IR beam, the intensity of the peak at 606 cm^{-1} becomes notably stronger. Minor variations can be observed at lower wavenumbers (peak at 580 cm^{-1} for slice 1 and peaks at 592 and 582 cm^{-1} for slice 2). Comparing Figure 4b with Figure 4d, it is evident that the spectral peak positions and

intensities in the 3000–4000 cm^{-1} range differ based on the crystal orientations of the samples. When IR light is incident parallel to the *c*-axis, the intensity of the absorption peak near 3039 cm^{-1} exceeds that near 3510 cm^{-1} . Conversely, when IR light is incident perpendicular to the *c*-axis, the intensity of the peak near 3039 cm^{-1} is much lower than that around 3512 cm^{-1} . This demonstrates the clear optical anisotropy in the infrared spectrum of apatite.

3.3. Electronic Spectral Characteristics of Alexandrite Effect Apatite

In gemmological research, UV-Vis and fluorescence spectroscopy are the two most frequently utilized electronic spectra. UV-Vis spectroscopy aids in defining the absorption traits of gemstones within the visible spectrum, offering insights into the origin of their colors [23–25]. Given that many naturally occurring gemstones exhibit fluorescence, fluorescence spectroscopy is invaluable for identifying them based on these properties. In this study, we employed visible absorption spectroscopy to delineate the absorption features of apatite in the visible spectrum. By correlating this with its chemical composition, we sought to shed light on the underlying causes of the alexandrite effect. Additionally, the luminescence of apatite was characterized using fluorescence spectroscopy, and the resulting data was interpreted in conjunction with the gemstone's rare-earth element content.

3.3.1. UV-Vis Spectra and the Alexandrite Effect Mechanism of Apatite

The term ‘alexandrite effect’ describes the unique phenomenon where specific minerals shift in appearance from blue–green in daylight to red under incandescent light. First observed in the early 19th century, this effect was characteristic of Cr-bearing alexandrites from the Ural Mountains. In recent times, this effect has also been noted in many varieties of gemstones. Minerals exhibiting the alexandrite effect have absorption spectra characterized by transmission peaks in the blue–green and red regions and a transmission dip in the yellow region. The observed colors for these minerals under the two transmission peaks are influenced by the greater transmittance of the blue–green section of the daylight spectrum (where blue and green are dominant) and the red segment under incandescent light (where red is more prominent).

For convenience, we denote the regions surrounding the transmission peaks as ‘transmission windows.’ To observe the alexandrite effect in gemstones, two criteria must be met: the presence of transmission windows in the blue–green and red areas, and the application of distinct light sources (namely the D65 light source for daylight and the A light source for incandescent light). To further understand the mechanisms driving the alexandrite effect, we delved into the UV-Vis spectra of apatite, illustrated in Figure 5. Figure 6 showcases the spectral relative power distribution for the D65 light source—simulating sunlight with a color temperature of 6500 K and the A light source that serves as a stand-in for incandescent lamps with a color temperature of 2856 K.

Figure 5 illustrates numerous absorption peaks in the UV-Vis spectra of apatite exhibiting the alexandrite effect. Distinct double absorption peaks appear at 748 and 738 nm, as well as 583 and 578 nm. There is also an absorption peak at 526 nm and minor absorption peaks at 514, 483, 473, 448, and 443 nm. Two transmission windows emerge flanking the double absorption peaks at 583 and 578 nm: transmission window A, on the left, mainly transmits yellowish-green light, while transmission window B, on the right, predominantly transmits pinkish-orange light. Transmission window A results from the combined effect of the double peaks at 583 and 578 nm and the peak at 526 nm. Transmission window B, more pronounced, arises from the double peaks at 583 and 578 nm coupled with another set of double peaks at 748 and 738 nm. It is worth noting that such absorption peaks are also present in the UV-Vis spectra of many typical yellow–green apatites that do not exhibit the alexandrite effect. However, these apatites have an additional absorption characteristic linked to a color center associated with Ce [6,21]. This absorption primarily occurs in the red-light region, negating the presence of transmission window B in that area. Hence, these yellow–green apatites do not showcase the alexandrite effect.

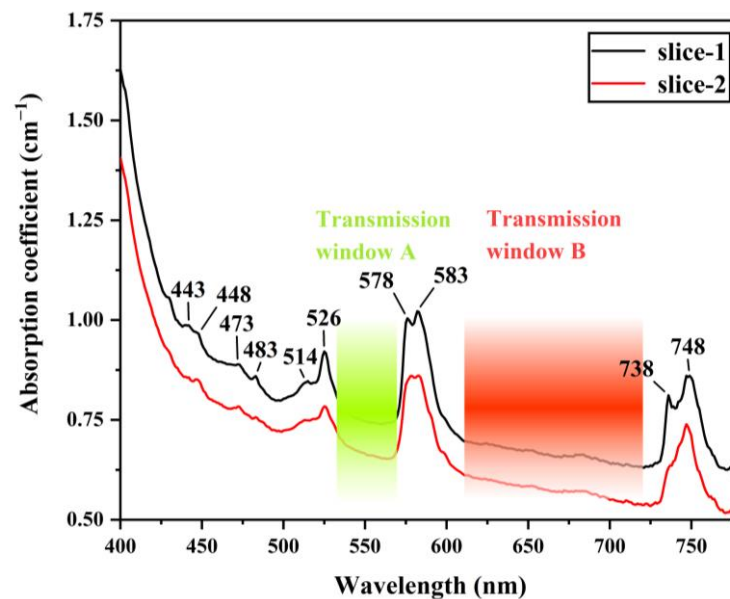


Figure 5. UV-Vis spectra of alexandrite effect apatite. There are two transmission windows in the visible region, which lead to the alexandrite effect of the apatite. Transmission window A is mainly located in greenish-yellow light region and transmission window B is mainly located in red light region.

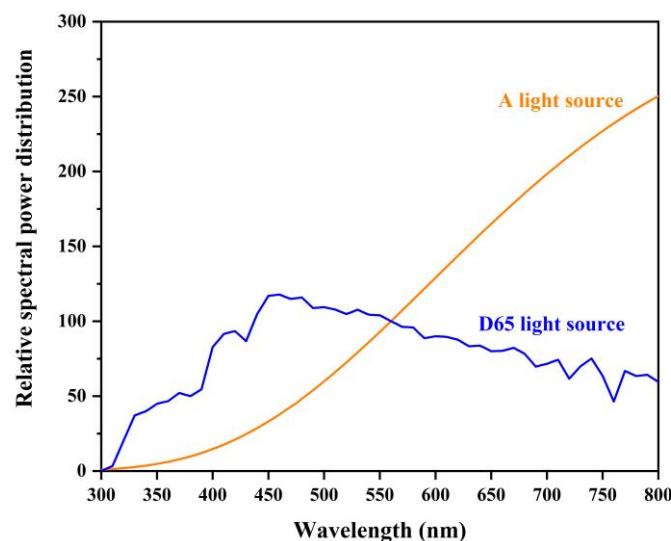


Figure 6. Spectral relative power distribution of D65 light source and A light source. The different intensity maxima (for D65 light source in the blue–green spectral region and A light source in the red spectral region) are very noticeable.

Referring to the relative spectral power distribution of the D65 light source shown in Figure 6, apatite with the alexandrite effect appears predominantly yellowish-green in daylight. This is because daylight allows for a higher transmission of light through transmission window A, corresponding to more yellow–green light passing through. By comparing this with the relative spectral power distribution of incandescent light in Figure 6, under incandescent lighting, the dominance of red light transition in transmission window B results in the apatite exuding an overall pink hue. Thus, the apatite’s alexandrite effect chiefly stems from absorption peaks at 748, 738, 583, 578, and 526 nm. Based on prior researches, these alexandrite effect peaks are all attributed to the light rare-earth element Nd [4–8,41]. This indicates that the light rare-earth element Nd is responsible for inducing the alexandrite effect in apatite.

3.3.2. Fluorescence Spectra of Alexandrite Effect Apatite

Natural apatite, primarily composed of calcium carbonate, is renowned for its luminescent properties. The application of fluorescence spectroscopy offers a swift and non-invasive approach to gemstone identification [24,25]. While several studies have delved into the fluorescence attributes of natural apatite, some of the literature specifically examines the impact of heat treatment on apatite's luminescence [6]. With an aim to establish a foundational understanding of its fluorescence characteristics, we gathered the fluorescence spectra of the apatite in question. We began by obtaining the three-dimensional excitation–emission matrix fluorescence spectra, depicted in Figure 7a,c. Utilizing this matrix, we identified the optimal excitation wavelength to be 296 nm. Subsequently, the fluorescence spectra were captured at this excitation wavelength and are presented in Figure 7b,d.

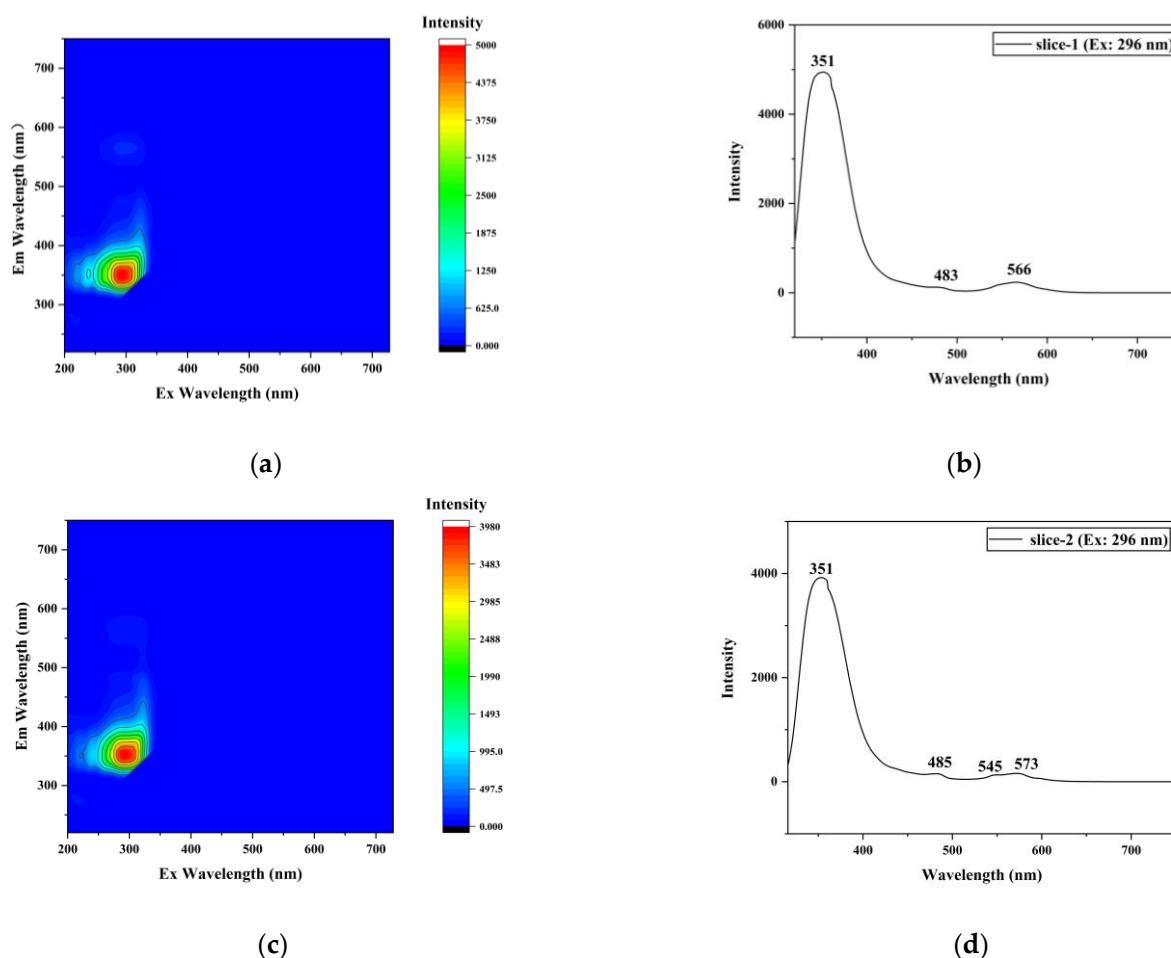


Figure 7. (a) Three-dimensional excitation–emission matrix fluorescence spectrum of slice-1. (b) Fluorescence spectra of sample slice-1 at 296 nm excitation wavelength. (c) Three-dimensional excitation–emission matrix fluorescence spectrum of slice-2. (d) Fluorescence spectra of sample slice-2 at 296 nm excitation wavelength.

In examining Figure 7a,c, the three-dimensional fluorescence spectra for both slices display strikingly similar characteristics. The most pronounced fluorescence is positioned at λ_{Ex} 296 nm/ λ_{Em} 351 nm. For slice-1, with an excitation wavelength of 296 nm, peaks are evident at 351, 483, and 566 nm, as depicted in Figure 7b. Conversely, slice-2 reveals nearly analogous peaks at 351, 485, 545, and 573 nm with the same excitation wavelength, as illustrated in Figure 7d. Drawing upon prior researches concerning apatite's fluorescence [42–45], the fluorescence peak at 351 nm can be attributed to Ce^{3+} within the apatite structure. The fluorescence peak around 483 nm is associated with Eu^{2+} , while the peak

around 566 nm is linked to both Nd^{3+} and Mn^{2+} . In summary, the defining peaks in apatite's fluorescence spectrum primarily arise from the presence of Ce, Eu, Nd, and Mn.

4. Conclusions

To date, apatite exhibiting the alexandrite effect has been exclusively discovered in the Akzhailyau Mountains of Kazakhstan, making it a rare gemstone in the market. Spectroscopic investigations on this apatite by gemologists remain limited. Consequently, a detailed spectroscopic analysis, a common practice in gemology, is crucial. In the Raman spectroscopy of the slice cut perpendicular to the crystal's c -axis, peaks appear at 1084, 1060, 1035, 965, 606, 580, and 448 cm^{-1} . Meanwhile, the slice cut parallel to the c -axis reveals peaks at 1083, 1053, 965, 606, 591, 452, and 430 cm^{-1} . All these peaks can be attributed to various vibrational modes of $[\text{PO}_4]^{3-}$. For infrared spectroscopy of the perpendicular cut, peaks within the $400\text{--}1300\text{ cm}^{-1}$ range are at 1095, 1051, 966, 606, and 580 cm^{-1} , whereas those within the $3000\text{--}4000\text{ cm}^{-1}$ range include 3589, 3510, 3482, 3117, 3091, and 3039 cm^{-1} . For the infrared spectrum of slice-2, peaks in the $400\text{--}1300\text{ cm}^{-1}$ range are 1092, 1045, 966, 606, 592, and 582 cm^{-1} , with 3568, 3547, 3512, 3482, 3117, and 3039 cm^{-1} in the $3000\text{--}4000\text{ cm}^{-1}$ range. Peaks from $400\text{--}1300\text{ cm}^{-1}$ relate to $[\text{PO}_4]^{3-}$ vibrational modes, while those from $3000\text{--}4000\text{ cm}^{-1}$ correspond to OH stretching vibrations. Both Raman and infrared spectroscopies indicate that apatite spectral peak positions vary with crystal orientations. Thus, for apatite jewelry identification, recognizing these nuanced differences due to crystal cutting direction is vital. The UV-Vis spectrum of apatite prominently features double absorption peaks at 748 and 738 nm, 583 and 578 nm, and a peak at 526 nm, all associated with the rare-earth element Nd. These absorption peaks generate one transmission window in the red-light region and another in the yellow–green light region, resulting in the alexandrite effect. This suggests that the alexandrite effect in apatite primarily originates from Nd. The two slices' three-dimensional fluorescence spectra display comparable characteristics, with the most intense fluorescence located at $\lambda_{\text{Ex}} 296\text{ nm}/\lambda_{\text{Em}} 351\text{ nm}$. With an optimal excitation wavelength of 296 nm, emission peaks at 351, 483, and 566 nm correlate to Ce^{3+} , Eu^{2+} , Nd^{3+} , and Mn^{2+} , respectively. Heat treatment is the prevalent technique for apatite processing. Using infrared, UV-Vis, and fluorescence spectroscopies provides powerful tools to study the heat treatment of alexandrite effect apatite. Exploring these spectral characteristics offers foundational knowledge to advance, refine, and identify heat treatment methods for this particular apatite.

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References

1. Hughes, J.M.; Cameron, M.; Crowley, K.D. Structural Variations in Natural F, OH, and Cl Apatites. *Am. Mineral.* **1989**, *74*, 870–876. [[CrossRef](#)]
2. Hughes, J.M.; Cameron, M.; Mariano, A.N. Rare-Earth-Element Ordering and Structural Variations in Natural Rare-Earth-Bearing Apatites. *Am. Mineral.* **1991**, *76*, 1165–1173. [[CrossRef](#)]
3. Hazrah, K.S.; Antao, S.M. Apatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH}, \text{F}, \text{Cl})_2$: Structural Variations, Natural Solid Solutions, Intergrowths, and Zoning. *Minerals* **2022**, *12*, 527. [[CrossRef](#)]

4. Gilinskaya, L.G.; Mashkovtsev, R.I. Blue and Green Centers in Natural Apatites by ERS and Optical Spectroscopy Data. *J. Struct. Chem.* **1995**, *36*, 76–86. [\[CrossRef\]](#)
5. Grisafe, D.A.; Hummel, F.A. Crystal Chemistry and Color in Apatites Containing Cobalt, Nickel, and Rare-earth ions. *Am. Mineral.* **1970**, *55*, 1131–1145.
6. Chindudsadeegul, P.; Jamkratoke, M. Effect of Heat Treatment on the Luminescence Properties of Natural Apatite. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2018**, *204*, 276–280. [\[CrossRef\]](#)
7. Roman-Lopez, J.; Correcher, V.; Garcia-Guinea, J.; Prado-Herrero, P.; Rivera, T.; Lozano, I.B. Effect of the Chemical Impurities on the Luminescence Emission of Natural Apatites. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2014**, *126*, 142–147. [\[CrossRef\]](#)
8. Cantelar, E.; Lifante, G.; Calderón, T.; Meléndrez, R.; Millán, A.; Alvarez, M.A.; Barboza-Flores, M. Optical Characterisation of Rare Earths in Natural Fluorapatite. *J. Alloys Compd.* **2001**, *323–324*, 851–854. [\[CrossRef\]](#)
9. Zharinov, A.A.; Ponomarenko, V.V.; Pekov, I.V. Color-Change Apatite from Kazakhstan. *Rocks Miner.* **2008**, *83*, 148–151. [\[CrossRef\]](#)
10. Gublein, E.J.; Schmetzer, K. Gemstones with Alexandrite Effect. *Gems Gemol.* **1982**, *18*, 197–203. [\[CrossRef\]](#)
11. Hainschwang, T. *Gemstone Analysis by Spectroscopy*, 3rd ed.; Elsevier Ltd.: Amsterdam, The Netherlands, 2016; ISBN 9780128032244.
12. Mercurio, M.; Rossi, M.; Izzo, F.; Cappelletti, P.; Germinario, C.; Grifa, C.; Petrelli, M.; Vergara, A.; Langella, A. The Characterization of Natural Gemstones Using Non-Invasive FT-IR Spectroscopy: New Data on Tourmalines. *Talanta* **2018**, *178*, 147–159. [\[CrossRef\]](#)
13. Barone, G.; Mazzoleni, P.; Raneri, S.; Jehlička, J.; Vandenabeele, P.; Lottici, P.P.; Lamagna, G.; Manenti, A.M.; Bersani, D. Raman Investigation of Precious Jewelry Collections Preserved in Paolo Orsi Regional Museum (Siracusa, Sicily) Using Portable Equipment. *Appl. Spectrosc.* **2016**, *70*, 1420–1431. [\[CrossRef\]](#)
14. Conti, C.; Botteon, A.; Bertasa, M.; Colombo, C.; Realini, M.; Sali, D. Portable Sequentially Shifted Excitation Raman Spectroscopy as an Innovative Tool for: In Situ Chemical Interrogation of Painted Surfaces. *Analyst* **2016**, *141*, 4599–4607. [\[CrossRef\]](#)
15. Izzo, F.; Germinario, C.; Grifa, C.; Langella, A.; Mercurio, M. External Reflectance FTIR Dataset (4000–400 cm^{−1}) for the Identification of Relevant Mineralogical Phases Forming Cultural Heritage Materials. *Infrared Phys. Technol.* **2020**, *106*, 103266. [\[CrossRef\]](#)
16. Lauwers, D.; Hutado, A.G.; Tanevska, V.; Moens, L.; Bersani, D.; Vandenabeele, P. Characterisation of a Portable Raman Spectrometer for in Situ Analysis of Art Objects. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2014**, *118*, 294–301. [\[CrossRef\]](#) [\[PubMed\]](#)
17. Mazzoleni, P.; Barone, G.; Raneri, S.; Aquilia, E.; Bersani, D.; Cirrincione, R. Application of Micro-Raman Spectroscopy for the Identification of Unclassified Minerals Preserved in Old Museum Collections. *Plinius* **2016**, *42*, 112–124. [\[CrossRef\]](#)
18. Patrizi, G.; Vagnini, M.; Vivani, R.; Fiorini, L.; Miliani, C. Archaeometric Study of Etruscan Scarab Gemstones by Non-Destructive Chemical and Topographical Analysis. *J. Archaeol. Sci. Reports* **2016**, *8*, 381–391. [\[CrossRef\]](#)
19. Rosi, F.; Cartechini, L.; Sali, D.; Miliani, C. Recent Trends in the Application of Fourier Transform Infrared (FT-IR) Spectroscopy in Heritage Science: From Micro: From Non-Invasive FT-IR. *Phys. Sci. Rev.* **2019**, *4*, 20180006. [\[CrossRef\]](#)
20. Miliani, C.; Rosi, F.; Daveri, A.; Brunetti, B.G. Reflection Infrared Spectroscopy for the Non-Invasive in Situ Study of Artists' Pigments. *Appl. Phys. A Mater. Sci. Process.* **2012**, *106*, 295–307. [\[CrossRef\]](#)
21. Zhang, J.; Shao, T.; Shen, A. The UV-Vis spectral Study on Thermal Treatment of Yellowish-Green Apatites. *Spectrosc. Spect. Anal.* **2020**, *40*, 147–151. (In Chinese) [\[CrossRef\]](#)
22. Chen, C.; Huang, W.; Gao, Q.; Fan, L.; Shen, A. Assignments on Raman Peaks of Red Coral Based on Experimental Raman Spectroscopy and Density Functional Theory Calculation. *Spectrosc. Spect. Anal.* **2021**, *41*, 127–130. (In Chinese) [\[CrossRef\]](#)
23. Chen, C.; Huang, W.; Shao, T.; Shen, C.; Li, Z.; Shen, A. The Study on UV-Vis Spectrum of a Special Color-Changed Sapphire. *Spectrosc. Spect. Anal.* **2019**, *39*, 2470–2473. (In Chinese) [\[CrossRef\]](#)
24. Zhang, Z.; Shen, A. Fluorescence and Phosphorescence Spectroscopies and Their Applications in Gem Characterization. *Minerals* **2023**, *13*, 626. [\[CrossRef\]](#)
25. Shao, T.; Lyu, F.; Guo, X.; Zhang, J.; Zhang, H.; Hu, X.; Shen, A.H. The Role of Isolated Nitrogen in Phosphorescence of High-Temperature-High-Pressure Synthetic Type IIb Diamonds. *Carbon* **2020**, *167*, 888–895. [\[CrossRef\]](#)
26. Chen, C.; Yu, J.; Zhang, C.; Ye, X.; Shen, A.H. Nature of Pigments in Orange and Purple Coloured Chinese Freshwater Cultured Pearls: Insights from Experimental Raman Spectroscopy and DFT Calculations. *Minerals* **2023**, *13*, 959. [\[CrossRef\]](#)
27. Chen, C.; Yu, J.; Ye, X.; Shen, A.H. Deciphering the Color Origin of Pink Conch Pearl Using Nondestructive Spectroscopies and DFT Calculations. *Minerals* **2023**, *13*, 811. [\[CrossRef\]](#)
28. Liu, Y.; Hu, Z.; Gao, S.; Günther, D.; Xu, J.; Gao, C.; Chen, H. In Situ Analysis of Major and Trace Elements of Anhydrous Minerals by LA-ICP-MS without Applying an Internal Standard. *Chem. Geol.* **2008**, *257*, 34–43. [\[CrossRef\]](#)
29. Fleet, M.E.; Pan, Y. Crystal Chemistry of Rare Earth Elements in Fluorapatite and Some Calc-Silicates. *Eur. J. Mineral.* **1995**, *7*, 591–606. [\[CrossRef\]](#)
30. Fleet, M.E.; Pan, Y. Site Preference of Rare Earth Elements in Fluorapatite. *Am. Mineral.* **1995**, *80*, 329–335. [\[CrossRef\]](#)
31. Ulian, G.; Valdré, G.; Corno, M.; Ugliengo, P. The Vibrational Features of Hydroxylapatite and Type A Carbonated Apatite: A First Principle Contribution. *Am. Mineral.* **2013**, *98*, 752–759. [\[CrossRef\]](#)
32. Klee, W.E. The Vibrational Spectra of the Phosphate Ions in Fluorapatite. *Zeitschrift für Krist. New Cryst. Struct.* **1970**, *131*, 95–102. [\[CrossRef\]](#)

33. Khan, A.F.; Awais, M.; Khan, A.S.; Tabassum, S.; Chaudhry, A.A.; Rehman, I.U. Raman Spectroscopy of Natural Bone and Synthetic Apatites. *Appl. Spectrosc. Rev.* **2013**, *48*, 329–355. [\[CrossRef\]](#)
34. Leroy, G.; Leroy, N.; Penel, G.; Rey, C.; Lafforgue, P.; Bres, E. Polarized Micro-Raman Study of Fluorapatite Single Crystals. *Appl. Spectrosc.* **2000**, *54*, 1521–1527. [\[CrossRef\]](#)
35. Yu, L.; Comodi, P.; Sassi, P. Vibrational Spectroscopic Investigation of Phosphate Tetrahedron in Fluor-, Hydroxy-, and Chlorapatites. *Neues Jahrb. fur Mineral. Abhandlungen* **1998**, *174*, 211–222. [\[CrossRef\]](#)
36. Comodi, P.; Liu, Y.; Frezzotti, M.L. Structural and Vibrational Behaviour of Fluorapatite with Pressure. Part II: In Situ Micro-Raman Spectroscopic Investigation. *Phys. Chem. Miner.* **2001**, *28*, 225–231. [\[CrossRef\]](#)
37. Becker, P.; Libowitzky, E.; Kleinschrodt, R.; Bohatý, L. Linear Optical Properties and Raman Spectroscopy of Natural Fluorapatite. *Cryst. Res. Technol.* **2016**, *51*, 282–289. [\[CrossRef\]](#)
38. Adams, D.M.; Gardner, I.R. Single-Crystal Vibrational Spectra of Apatite, Vanadinite, and Mimetite. *J. Chem. Soc. Dalt. Trans.* **1974**, *14*, 1505–1509. [\[CrossRef\]](#)
39. Chen, Q.Q.; Hu, C.L.; Yao, L.J.; Chen, J.; Cao, M.Y.; Li, B.X.; Mao, J.G. $\text{Cd}_2(\text{IO}_3)(\text{PO}_4)$ and $\text{Cd}_{1.62}\text{Mg}_{0.38}(\text{IO}_3)(\text{PO}_4)$: Metal Iodate-Phosphates with Large SHG Responses and Wide Band Gaps. *Chem. Commun.* **2022**, 7697, 7694–7697. [\[CrossRef\]](#)
40. Qiu, H.; Li, F.; Jin, C.; Lu, J.; Yang, Z.; Pan, S.; Mutailipu, M. $(\text{N}_2\text{H}_6)[\text{HPO}_3\text{F}]_2$: Maximizing the Optical Anisotropy of Deep-Ultraviolet Fluorophosphates. *Chem. Commun.* **2022**, *58*, 5594–5597. [\[CrossRef\]](#)
41. Fleet, M.E.; Pan, Y. Site Preference of Nd in Fluorapatite $[\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2]$. *J. Solid State Chem.* **1994**, *112*, 78–81. [\[CrossRef\]](#)
42. Czaja, M.; Bodył, S.; Lisiecki, R.; Mazurak, Z. Luminescence Properties of Pr^{3+} and Sm^{3+} Ions in Natural Apatites. *Phys. Chem. Miner.* **2010**, *37*, 425–433. [\[CrossRef\]](#)
43. Lyon, B.; Luminescents, P.M. Luminescence of Eu(III), Pr(III) and Sm(III) in Carbonate-Fluor-Apatite. *Acta Phys. Pol. A* **1996**, *90*, 267–274. [\[CrossRef\]](#)
44. Gaft, M.; Shoval, S.; Panczer, G.; Nathan, Y.; Champagnon, B.; Garapon, C. Luminescence of Uranium and Rare-Earth Elements in Apatite of Fossil Fish Teeth. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **1996**, *126*, 187–193. [\[CrossRef\]](#)
45. Gaft, M.; Reisfeld, R.; Panczer, G.; Shoval, S.; Champagnon, B.; Boulon, G. Eu^{3+} Luminescence in High-Symmetry Sites of Natural Apatite. *J. Lumin.* **1997**, *72–74*, 572–574. [\[CrossRef\]](#)

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