Research Article

Characterization of Blue Tourmaline from Madagascar for Exploring Its Color Origin

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In the research, spectroscopic studies of tourmaline for color origin were performed by X-ray diffraction, Fourier transform infrared spectroscopy, ultraviolet-visible spectroscopy, and X-ray photoelectron spectroscopy. The research work emphasized the analysis of transition metal atoms, including their valence state and coordination number, in order to better understand the effect of transition metal cations on the color origin. The results showed that the blue color of the crystal is caused by the strong absorption at 725 nm in the red spectrum, which generates a symmetrical and wide absorption band. The absorption band at 725 nm is caused by charge transfer between Fe$^{2+}$ at the Y site and Fe$^{3+}$ at the Z site. Other ions in the crystal did not generate absorption lines in the visible spectral range. Besides position, its valence state and coordination number were clarified to reveal color variation and the origin of tourmaline. Most importantly, this spectroscopic analysis method makes the coloration mechanism of charge transfer that is difficult to be uncovered to be clearly revealed, which will provide an available material and chemical method to investigate the structure-property relationship for gems as well as reveal the genesis of beautiful colors.

1. Introduction

Tourmaline is a naturally occurring borosilicate mineral with good piezoelectricity, pyroelectricity, and spontaneous polarity. It has important applications in many fields, such as radio, infrared detection, and refrigeration [1, 2]. The brightly colored, clear, and transparent tourmaline is used as a raw material for gemstones [3]. The color of tourmaline is the key to whether it can make a gemstone. Pure tourmaline is colorless, but it often has a wide variety of colors, such as rose or pink, red, yellow, green, blue, purple, and black, according to its composition. Iron-rich tourmaline is dark green, dark blue, dark brown, or black; magnesium-rich tourmaline appears yellow or brown; tourmaline is rich in lithium and manganese and is rose or light blue; chromium-rich tourmaline is dark green [4]. With a very complex chemical composition, the crystal-chemical formula of tourmaline is $XY_3Z_6[Si_6O_{18}][BO_3]_3\text{V}_3W$, in which $X=\text{Na}^+$, $\text{Ca}^{2+}$, and an unoccupied site; $Y=\text{Li}^+$, $\text{Mg}^{2+}$, and $\text{Fe}^{3+}$, $\text{Mn}^{2+}$, $\text{Al}^{3+}$, $\text{Cr}^{3+}$, $\text{V}^{3+}$, and $\text{Fe}^{3+}$; $Z=\text{Mg}^{2+}$, $\text{Al}^{3+}$, $\text{Fe}^{3+}$, $\text{V}^{3+}$, and $\text{Cr}^{3+}$; $V=\text{OH}$ and $O$; and $W=\text{OH}$, $F$, and $O$. At different sites in the crystal structure of tourmaline, there are extensive isomorphic substitutions that contribute to the formation of elbaite, dravite, schorl, and other species [5]. Previous reports found that trace transition metal elements resulted in the apparent color of tourmaline [6]. Colorless tourmaline contains zero or small amounts of transition elements [7]. The pink color can be induced by the d-d electron transition of $\text{Mn}^{3+}$ at the octahedral site [8]. The red color is due to the combined effects of $\text{Mn}^{2+}$ and $\text{Fe}^{3+}$ [9], and the green color can be attributed to the combined action of $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ [10]. According to previous research, the occupancy and coordination environment of atoms in the crystal lattice had an obvious influence on the apparent color of tourmaline [11–13]. Although there are many studies on the spectroscopic characteristics of tourmaline and the origin of their colors, they mainly focused on tourmalines with bright colors, such as red, green, and neon blue. In addition, their research methods focused mainly on the spectral line characteristics of transition metal cations [14], or the change in absorption line characteristics with the change in ion states [15, 16]. A few studies have been conducted on dark
toumalines, such as blue and purple, and the influence of the occupancy and coordination environment of transition metal ions on the color. This study examined the relationship between the chemical state of the color-causing ions and coloration by analyzing the spectroscopic characteristics of dark blue tourmaline from Madagascar. The results will provide a reliable theoretical basis for the color optimization of tourmaline, which will be useful for identifying the origin of tourmaline gemstones.

2. Materials and Methods

Powder (Figure 1(a)), faceted stones (Figure 1(b)), and crystal fragments with fresh fractures (Figure 1(c)) were used in experiments. Samples were all prepared from natural dark blue raw tourmalines mined in Madagascar. All chemicals used in the experiments were of analytical grade and used as received.

Faceted gemstones were used for refractive index testing, and crystal fragments with fresh fractures were used for Mohs hardness testing. The powder was characterized by X-ray diffraction (XRD, Bruker D8 Advance) with a scan range from 5° to 65° and Fourier transform infrared (FTIR, Bruker Vertex 80) spectroscopy using the KBr pellet method in transmission mode between 4000 and 400 cm\(^{-1}\). In ultraviolet-visible spectroscopy (UV-Vis JASCO MSV5200) characterization, the faceted stones were involved. The test was in transmission mode, in which the range was set from 380 to 1000 nm, with a resolution of 1 nm and a scanning speed of 2000 nm/min. In X-ray photoelectron spectroscopy (XPS) characterization, fresh fragments of the crystal were used to avoid contamination, which were enwrapped with tinfoil and were then broken by a pair of pincers immediately before the XPS measurement. Detailed conditions were as follows: Al K\(_\alpha\) (E = 1486.6 eV) X-ray radiation source, instrument vacuum better than 5 × 10\(^{-7}\) Pa, scanning step length of 0.05 eV, and counting time of 500 ms. In the XPS characterization, fine scanning of the C1s electron binding energy value (284.8 eV) was used for equipment calibration.

3. Results and Discussion

3.1. Gemological Characteristics. The Mohs hardness of the crystal is 7.5. Refractometer tests showed that the index of refraction of the crystal was Ne = 1.624, No = 1.644.

3.2. X-ray Diffraction Analysis. The XRD pattern of the dark blue tourmaline from Madagascar was presented in Figure 2.

The strongest XRD d-spacings were 6.391 (101), 4.986 (021), 4.230 (211), 4.008 (220), 3.464 (012), 2.952 (122), 2.578 (051), 2.038 (152), 1.654 (603), and 1.448 (514) Å. The pattern indicates that it is schoenite by comparison with the XRD standard card (PDF4i-1497). The sharp and symmetrical XRD peaks indicated that the crystallinity was good. The information contained in the geometrical crystal structure was calculated by least square extrapolation with the help of software (XrayRun2020). The result was that the crystal exhibited a relatively simple, highly symmetrical trigonal structure with the space group R3 m and its lattice constants were a\(_0\) = 15.9526 and c\(_0\) = 7.1360 Å.

3.3. FTIR Spectroscopy Analysis. Figure 3 presents the FTIR spectrum of the dark blue tourmaline from Madagascar. Except for a slight difference in absorption peaks at 451 and 848 cm\(^{-1}\), the peaks of the FTIR spectrum are similar to that of tourmaline [17].

The FTIR absorption peak of 451 cm\(^{-1}\) in Figure 3 was assigned to the vibration of the [MO\(_6\)] bond, which is rare or weak within 400–500 cm\(^{-1}\) in other FTIR spectrums of tourmalines. Generally, metal cations include Fe, Mg, and Al, while the vibration absorption peak of Mg-O and the vibration absorption peak of Fe-O are assigned to 470 cm\(^{-1}\) and 400 cm\(^{-1}\), respectively [18]. On account of the characteristics of Fe, Mg, and Al and their occupancy in the crystal structure, the absorption peak at 451 cm\(^{-1}\) may be attributed to the vibration of the coordination polyhedron Al-O in [AlO\(_4\)] [19].

In the range of 500–1110 cm\(^{-1}\), a large number of symmetrical absorption peaks, namely, at 507, 632, 718, 750, 783, 848, 985, 1023, and 1105 cm\(^{-1}\), was found to reflect the vibration of the [Si\(_6\)O\(_{18}\)] group. Other absorption peaks were attributed as follows: the peak at 507 cm\(^{-1}\) belonging to the bending vibration (δSi-O) of Si-O, the absorption peaks at 632, 718, 750, and 783 cm\(^{-1}\) belonging to the symmetrical stretching vibration (νSi-O-Si) of Si-O-Si in the [Si\(_6\)O\(_{18}\)] group, the peak at 848 cm\(^{-1}\) belonging to the symmetric stretching vibration (νSi-O-Si) of Si-O-Si, the peak at 985 cm\(^{-1}\) belonging to the symmetric stretching vibration (νSi-O-Si) of O-Si-O, the absorption peak at 1023 cm\(^{-1}\) belonging to the asymmetric stretching vibration (νasSi-O-Si) of O-Si-O, the peak at 1105 cm\(^{-1}\) belonging to the asymmetric stretching vibration (νasSi-O-Si) of O-Si-O, the peak at 1297 cm\(^{-1}\) and 1343 cm\(^{-1}\) belonging to the stretching vibration (νBO\(_3\)) of [BO\(_4\)] and the bending vibration (δOH) of OH, respectively, the vibrational absorption band of 3000–3800 cm\(^{-1}\) belonging to the H bond from water, peaks at 3494 cm\(^{-1}\) and 3561 cm\(^{-1}\) belonging to the vibration (νO3H) of O3H, and a weaker absorption band at 3597 cm\(^{-1}\) belonging to the vibration (νO1H) of O1H [20–22].

3.4. UV-Vis Spectroscopy. The dark blue color was a special feature of blue tourmaline from Madagascar. The color structure and absorption bands for the dark blue color were found in the UV-Vis absorption spectrum. As shown in Figure 4, the sample forms only one typical absorption peak in the visible spectrum (390–780 nm), i.e., a broad and strong absorption peak with good symmetry was formed at 725 nm in the red region of the spectrum.

A dark blue color is the result of typically absorbed red wavelengths and transmitted blue wavelengths. However, researchers have controversy regarding the cause of the absorption peak at 725 nm. Grum-Grzhimailo attributed the peak near 718 nm to Mn\(^{3+}\), while Wilkins et al. attributed it to Fe\(^{3+}\) [9, 23]. Smith et al. suggested that the peak is partially
caused by the spin-allowed transition of Fe$^{2+}$, mainly due to charge transfer between Fe$^{2+}$ and Fe$^{3+}$, which are accommodated at different octahedral sites with shared edges and tops [24, 25]. This charge transfer can cause strong absorption, which would become more obvious with increasing concentration. By contrast, Hush, Fritsch, and Fan Jianliang attributed the peak to the charge transfer of Fe$^{2+}$–Fe$^{3+}$ [10, 26, 27]. Furthermore, more chemical data on tourmaline are needed to clarify extensive isomorphic substitution in tourmaline crystals and the vital contribution of variable-valence elements to tourmaline coloration. Therefore, the XPS characterization was used.

3.5. XPS Analysis. First, the sample was subjected to a broad-spectrum scan to determine the elemental species in the sample. A detailed scan of the sample was then performed to investigate the chemical states of the transition metals. Figure 5 shows the broad XPS spectrum.

The overall XPS spectrum showed that there are mainly B, O, F, Na, Al, Si, Fe, and other elements in the dark blue tourmaline. The high-resolution XPS spectra (Figure 6) showed that the dark blue tourmaline also contains a small amount of Mn in addition to Fe.

Factors, such as trace transition metal cations, the coordination environment with anions, and the chemical states

![Figure 1: Tourmaline samples: (a) powder, (b) faceted stones, and (c) crystal fragments.](image1)

![Figure 2: XRD pattern of the tourmaline sample.](image2)
of these transition metals, will change the color of tourmaline [13, 28, 29]. Figure 6 is the high-resolution XPS survey of transition metals. X—_he peak for Fe2p3/2 was asymmetric, with two prominent shoulder peaks on the high binding energy side, indicating that the Fe2p3/2 peak is a composite type (Figure 6(a)). Peak fitting revealed peaks at 709.2, 710.7, and 713.7 eV, which were assigned to the binding energies of Fe2p3/2 for FeO, Fe2O3, and FeF3, respectively (reference: 709.3, 710.8, and 713.9 eV for FeO, Fe2O3, and FeF3, respectively) [30–32]. X—_his indicates that the Fe in the dark blue tourmaline sample from Madagascar has two valence states: Fe2+ and Fe3+. Fe2+ bonds mainly with O, while Fe3+ bonds mainly with O and F.

XPS showed that the sample contains Fe and Mn; Mn exists as Mn2+, and Fe is in the form of Fe2+ and Fe3+. According to the characteristics of the crystal-chemical formula of tourmaline, it can be inferred that Mn2+ and Fe3+ occupy the Y site, and Fe2+ occupies the Z site. However, Fe3+ coordinates with F in the sample. From the previous research, F was found to only occupy the W site, and the ions at the W lattice site were found to only coordinate and bond with ions at the Y site instead of the Z site [34]. Therefore, Fe3+, which coordinates and bonds with ions at the F site, occupies the Y site, not the Z site. Table 1 lists the coordination of transition metal ions and their occupancy in the lattice.

The XPS spectrum of Mn2p is shown in Figure 6(b). In contrast to the Fe2p3/2 peak, the peak of Mn2p3/2 is highly symmetric and appears at 641.4 eV, corresponding to the electronic binding energy of Mn2p3/2 in MnO (641.5 eV). This indicates that Mn exists as Mn2+ and mainly bonds with O in the sample [29, 33].

XPS showed that the sample contains Fe and Mn; Mn exists as Mn2+, and Fe is in the form of Fe2+ and Fe3+. According to the characteristics of the crystal-chemical formula of tourmaline, it can be inferred that Mn2+ and Fe3+ occupy the Y site, and Fe2+ occupies the Z site. However, Fe3+ coordinates with F in the sample. From the previous research, F was found to only occupy the W site, and the ions at the W lattice site were found to only coordinate and bond with ions at the Y site instead of the Z site [34]. Therefore, Fe3+, which coordinates and bonds with ions at the F site, occupies the Y site, not the Z site. Table 1 lists the coordination of transition metal ions and their occupancy in the lattice.

Transition metal cations, including Mn2+, Fe2+, and some Fe3+, occupy the Y site in the crystal structure. Other Fe3+ cations occupy the Z site, which may result in some distortion of the [YO4VW] and [ZO5V] octahedrons, leading to a slight change in the closely connected [Si6O18] group structure. This is consistent with the appearance of special absorption peaks, such as 848 cm−1 in the FTIR spectrum. The color of the tourmaline crystal is mainly caused by the d-electron transition of ions at the Y and Z sites and the charge transfer between the ions sharing edges at the Y and Z sites [28, 29]. On the contrary, other studies believe that color is more associated with the nature of ions at the Y site [35]. According to the spectral
characteristics of dark blue tourmaline from Madagascar, the ion species, and their occupancy in the crystal structure, the color of the dark blue tourmaline was attributed to charge transfer between Fe$^{2+}$ occupying the Y site and Fe$^{3+}$ occupying the Z site. In other words, the Fe$^{2+}$–Fe$^{3+}$ charge transfer causes an absorption peak at 725 nm, which is broad and strong.

<table>
<thead>
<tr>
<th>Binding configurations</th>
<th>Estimated atomic percentages (%)</th>
<th>Site</th>
</tr>
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<tbody>
<tr>
<td>Fe$^{2+}$—O</td>
<td>19.6</td>
<td>Y</td>
</tr>
<tr>
<td>Fe$^{3+}$—O</td>
<td>39.4</td>
<td>Z</td>
</tr>
<tr>
<td>Fe$^{3+}$—F</td>
<td>41.0</td>
<td>Y</td>
</tr>
<tr>
<td>Mn$^{2+}$—O</td>
<td>100</td>
<td>Y</td>
</tr>
</tbody>
</table>

Table 1: Different binding configurations, estimated atomic percentages, and occupancy sites of Fe and Mn.
4. Conclusion

The blue tourmaline from Madagascar is Schorl, featuring absorption peaks at 451 and 848 cm\(^{-1}\) in the infrared spectrum. The dark blue color of tourmaline is caused by the strong absorption of visible light at 725 nm in the red spectrum, which generates a symmetrical and broad absorption band. Tourmaline contains transition metal cations, Fe\(^{2+}\), Mn\(^{2+}\), Fe\(^{3+}\), of which Fe\(^{2+}\), Mn\(^{2+}\), and some Fe\(^{3+}\) cations occupy the Y site in the crystal structure and another part of the Fe\(^{3+}\) cations occupying the Z position. The absorption band at 725 nm was assigned to charge transfer between Fe\(^{2+}\) occupying the Y site and Fe\(^{3+}\) occupying the Z site. The other ions in the crystal do not generate absorption lines in the visible spectrum.

Data Availability

The data are presented directly in the present study.

Conflicts of Interest

The author declares that there are no conflicts of interest.

Acknowledgments

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References

[1] F. Ren, Studies on Characteristics, Processing and Utilization of Inner Mongolian Tourmaline, Northeastern University, Shenyang, China, 2005.


