Research Article

The Chemical States of Color-Induced Cations in Tourmaline Characterized by X-Ray Photoelectron Spectroscopy

Ming Li,^{1,2} Hanlie Hong¹, ,¹ Ke Yin,¹ Chaowen Wang,³ Feng Cheng,¹ and Qian Fang¹

¹School of Earth Sciences, China University of Geosciences, Wuhan, China

²Department of Gemmology, Jinling Institute of Technology, Nanjing, China

³Gemmological Institute, China University of Geosciences, Wuhan, China

Correspondence should be addressed to Hanlie Hong; honghl8311@aliyun.com

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In order to better understand the effect of transition metal cations on color of tourmaline, X-ray photoelectron spectroscopy was used to investigate the species, chemical state, site occupancy, and chemical environment of color-induced metal cations in colorful tourmaline samples from Minas Gerais State, Brazil. Our results showed that the colorful tourmalines usually contained a small amount of transition metal elements, and a colorful tourmaline sample had several transition metal cations; however, the color of tourmaline resulted from the transition metal cations in the Y site of the crystal structure. The pink color of tourmaline was associated with Mn^{2+} in the Y site coordinating with F; the yellow color was derived from Ni^{2+} in the Y site binding to O; the green color was associated with Fe^{3+} in the Y site coordinating with O, OH, and F; the rose red color originated from Mn^{2+} and Ni^{2+} in the Y site in which Mn^{2+} coordinated with O and F, and Ni^{2+} coordinated with O; and the blue color was derived from Fe^{3+} and Mn^{2+} in the Y site in which Fe^{3+} binded to O, OH, and F and Mn^{2+} binded to F. Additionally, other transition metal cations were also observed in colorful tourmalines, but all these species occupied the Z site of the structure. In the pink and yellow samples, Fe and Cr were observed in Fe^{3+} and Cr^{3+} ; in the rose red sample, Fe was also found in Fe^{3+} ; in the blue sample, Cr was present in Cr^{3+} ; in the green sample, Mn, Ni, and Cu were found in Mn^{2+} , Ni^{2+} , and Cu^{2+} , respectively. The color of tourmaline was induced from the absorption of the d-d transition of transition metals in the crystal structure, as charge transfer tended to occur between cations occupying different coordination positions.

1. Introduction

Tourmaline, commonly known as “Bixi” in China, is a precious medium-high-grade gem material. It is termed the “fallen rainbow” and valued by consumers for its extremely rich and unique colors. Tourmaline is a polar silicate mineral crystal with no center of symmetry and has complex chemical compositions. Fluorine, hydroxyl, and other anions in addition to the silicate root are often found with boric acid and cations in the structure, such as Cr, Mn, and Fe, which have a wide range of isomorphic replacement. Tourmaline colors are extremely rich and variable [1–8]. Tourmaline can be colorless, pink, rose red, red, yellow, brown, green, dark green, light blue, blue, purple, and black, with color changes associated with variable chemical compositions. The mechanism that determines the color of tourmaline has been a perennial

problem in mineralogy. For example, some researchers believe that pink originated from the absorption of d-d transition of Mn in the octahedron, while others hypothesize it is the result of a color heart, similar to smoky quartz [9]. However, Chaudhry and Howie [10] did not find Mn when analyzing pink tourmaline from Devonshire, which rebuts the hypothesis that pink is caused by the absorption of the d-d transition of Mn^{3+} . Babińska et al. [11] used electron paramagnetic resonance (EPR) to identify Mn^{2+} in elbaite, Fe^{3+} in dravite and schorl. They also found that the color and spectral characteristic of tourmaline that contains Fe did not change regularly with varied Fe contents. This phenomenon suggests that the color of those tourmaline results from the charge transfer between Fe^{2+} and Fe^{3+} [12, 13]. Through research on pink and green tourmaline using the XPS (X-ray photoelectron spectroscopy) method, Hong et al. [14] hypothesized that

transition metal cations in different colored tourmalines have the same chemical state, for example, Fe^{3+} , Mn^{4+} , Ti^{4+} , and Cr^{3+} , but with different coordination ions. That may be the primary reason for the color difference. Petrov [15] showed that the violet color in tourmaline is caused by the absorption of the d-d transition for Cr^{3+} . A large number of studies have shown that the varied color in tourmaline is related to the various transition metal cation species, especially the state of these cations. However, researchers still have differing opinions on the attribution of the absorption belt, chemical state of the ions, and color mechanism [16, 17]. This study researched the chemical states of metal cations using X-ray photoelectron spectroscopy and explored the species, valence state, and especially coordination ion and site occupancy of color-induced metal cations, in pink, yellow, green, rose red, and blue tourmaline.

2. Materials and Methods

Six pieces of tourmaline, representative of different colors, were selected as samples from Minas Gerais, Brazil (Figure 1). Five samples were colored pink, yellow, green, rose red, and blue, and one colorless sample was chosen as the baseline sample.

Photoelectron spectroscopy can provide both qualitative and quantitative results, including the chemical state of the surface elements of the sample by testing the kinetic energy of the photoelectron and Auger electrons emitted from the solid surface from the photoelectric and Auger effects. This series of experiments was conducted on an AXIS-ULTRA DLD-600W X-ray photoelectron spectrometer at the Huazhong University of Science and Technology Analysis and Testing Center. In order to avoid contamination, the crystal sample was enwrapped with tinfoil and was then broken by a pair of pincers, and the fresh surface was subsequently used for XPS measurement. Test conditions were as follows: Al K α ($E = 1486.6$ eV) X-ray radiation source, instrument vacuum better than 5×10^{-9} Torr, scanning step length of 0.05 eV, and counting time of 500 ms. The charge displacement is fixed, and the C1s electron binding energy value (285 eV) was used for equipment calibration. The range of energy spectrum was 0–1200 eV. Because the subject of analysis was primarily trace elements, we carefully scanned the photoelectron spectra of these trace elements and repeated 15 times to improve the resolution.

For X-ray diffraction (XRD) analysis, the tourmaline sample was broken and further ground manually to powder using an agate mortar. XRD measurement was performed in a Philips PW 3710 diffractometer operated at CuK α radiation (45 kV, 35 mA) and scan rate of $4^\circ 2\theta/\text{min}$ at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences (Wuhan).

3. Results and Discussion

3.1. Crystal Chemistry of Tourmaline. The X-ray photoelectron spectroscopy results for the tourmaline samples are shown in Figure 2. Based on the standard electron binding energy data of the elements, although the tourmaline samples

FIGURE 1: Tourmaline samples.

differ in color, their main chemical components are similar; they all contain Al, Si, Na, O, F, B, and other elements. Results from the further slow scan confirm that these tourmaline samples also contain a small amount of Cr, Mn, Fe, Ni, and Cu, and other elements, but no Li or Be.

Tourmaline is a ring borosilicate mineral; its crystal chemical formula is generally recognized as $[18] \text{XY}_3\text{Z}_6[\text{T}_6\text{O}_{18}][-\text{BO}_3]_3\text{V}_3\text{W}$, where the X site is primarily occupied by large radius metal cations, such as Na^+ , K^+ , and Ca^{2+} . Sometimes, Mg^{2+} or a vacancy can be found in the X site. Its coordination number is 9. The Y site is occupied by Al^{3+} , Fe^{3+} , V^{3+} , Cr^{3+} , Mg^{2+} , Mn^{2+} , Fe^{2+} , Cu^{2+} , Zn^{2+} , Li^+ , and Ti^{4+} ; it can also contain some vacancies and has a coordination number of 6 [19]. The Z site is occupied by Al^{3+} , Fe^{3+} , V^{3+} , Cr^{3+} , Mg^{2+} , and Fe^{2+} and has a coordination number of 6. The T site is occupied by Si, can be partly replaced by Al, B, and Be, and has a coordination number of 4. The coordination number of B is 3, and there is no clear substitution. The W (O1) site is occupied by OH, F, and O and has a coordination number of 3. The V (O3) site is occupied by OH and O and has a coordination number of 3 [20].

In the tourmaline structure, the $[\text{TO}_4]$ tetrahedron forms $[\text{T}_6\text{O}_{18}]^{12-}$ a hexagonal ring. In comparison, the cation occupying the Y position of the crystal structure forms a brucite structure with O^{2-} , OH^- , and F^- . Three $[\text{Y-O}_4\text{VW}]$ coordination octahedrons are connected to the hexagonal ring by sharing an O^{2-} on the top of $[\text{TO}_4]$. The intersection of the three octahedrons lies on the central axis of the hexagonal ring, which is the W position. $[\text{BO}_3]$ is found between the six square rings and octahedral layer, which shares one O^{2-} with the octahedral layer. These complex anions are connected to each other by Z ions. The $[\text{Z-O}_5\text{V}]$ octahedron and $[\text{Y-O}_4\text{VW}]$ octahedron share one edge [21]. The X ions are located in the upper space of the hexagonal. Bosi [7] has shown that the W (O1) anion is mainly bonded to the metal cation in the Y site of the tourmaline crystal structure. Therefore, the metal cation in the Y site is mainly coordinated with the W (O1) anion, while the metal cation in the Z site does not bind to the W (O1) anion.

3.2. The Chemical State of Trace Elements. The tourmaline color is often associated with a very small amount of metal cations [22]. The fine analysis results showing the characteristic energy spectra for the metal cations are shown in Figures 3–7.

FIGURE 2: X-ray photoelectron spectra of tourmaline samples.

FIGURE 3: XPS spectra for Fe2p.

FIGURE 4: XPS spectra for Mn.

FIGURE 5: XPS spectra for Cr2p.

Figure 3 shows the XPS spectrum for Fe2p. The peaks of the energy spectrum line for the pink, yellow, and blue samples are clearly higher than those of colorless, green, and rose red samples. The peak heights reflect the abundance of Fe in tourmaline crystal. Therefore, the abundance of Fe in the pink, yellow, and blue samples is clearly higher than in the colorless, green, and rose red samples. For the colorless contrast sample, there is no significant spectral peak, indicating the lack of Fe. Furthermore, different samples have different

FIGURE 6: XPS spectra for Ni2p.

FIGURE 7: XPS spectrum for Cu2p.

peak positions. The Fe2p3/2 peaks of these samples show clearly an asymmetric shape, with one shoulder peak in the higher binding energy side, suggesting that the Fe2p3/2 line is an overlapping peak. By fitting calculation [23], the peak was decomposed into two peaks at 710.5 and 711.7 eV for the pink sample, at 710.6 and 711.7 eV for the yellow sample, at 711.3 and 713.1 eV for the green sample, and at 710.6, 711.3, and 713.1 eV for the blue sample, respectively. For the rose red sample, the Fe2p3/2 signal is significantly weak and is present as a single peak at 711.3 eV.

The different binding configurations and estimated percentages of Fe are reported in Table 1. The electron binding energies of Fe2p3/2 in Fe₂O₃, FeOOH, and NaFeO₂ are 710.7, 711.3, and 711.8 eV, respectively. In the pink, yellow, and blue samples, the electron binding energy of the

TABLE 1: Different binding configurations, estimated atomic percentages, and occupancy site of Fe, Mn, Cr, and Ni.

(a)					
	Fe ³⁺ —O	Fe ³⁺ —O +OH	Fe ³⁺ —O(—Na)	Fe ³⁺ —F	Site
Pink	66%	/	34%	/	Z
Yellow	65%	/	35%	/	Z
Green	/	82%	/	18%	Y
Rose red	/	100%	/	/	Z
Blue	48%	43%	/	9%	Y

(b)			
	Mn ²⁺ —O	Mn ²⁺ —F	Site
Pink	/	100%	Y
Green	100%	/	Z
Rose red	41%	59%	Y
Blue	/	100%	Y

(c)			
	Cr ³⁺ —O	Cr ³⁺ —O(—B)	Site
Pink	64%	36%	Z
Yellow	60%	40%	Z
Blue	/	100%	Z

(d)			
	Ni ²⁺ —O	Ni ²⁺ —O(—Al)	Site
Yellow	/	100%	Y
Green	100%	/	Z
Rose red	/	100%	Y

strongest Fe2p3/2 component are 710.5, 710.6, and 710.6 eV, respectively, coinciding with the electron binding energy of Fe2p3/2 in Fe₂O₃, indicating that Fe is mainly in the Fe³⁺ chemical state and coordinates with O. The Fe2p3/2 peak at 711.7 eV for pink and yellow samples is approximately consistent with the electron binding energy of Fe2p3/2 in NaFeO₂, indicating that part of Fe coordinates with O and O also binds with Na in the crystal structure of these samples. The binding energy of Fe2p3/2 in the rose red sample is 711.3 eV, in agreement with the electron binding energy of Fe2p3/2 in FeOOH, indicating that Fe mainly bonds with O and OH. However, the electron binding energy of Fe2p3/2 at 713.1 eV in the green and blue samples is slightly lower than the value 713.9 eV for Fe2p3/2 in FeF₃ [24], indicating that Fe is in the Fe³⁺ chemical state and mainly bonds with F, O, and OH. The relative proportion of Fe in different coordinate states is listed in Table 1.

The colorless, rose red, and blue samples show extremely weak Mn2p peaks, while the pink and green samples have an obvious Mn2p peak, indicating that the colorless, rose red, and blue samples contain significantly a small amount of Mn in the crystals compared to the pink and green samples

(Figure 4). The Mn2p peaks exhibit generally symmetric shapes for pink, green, and blue samples, and the Mn2p electron binding energy is 640.8 eV for the green sample and 642.6 eV for pink and blue samples. On the contrary, the Mn2p_{3/2} peak of the rose red sample is asymmetric, which is decomposed into two peaks at 640.8 and 642.6 eV, respectively, by peak fitting.

The different binding configurations and estimated percentages of Mn in various chemical states are reported in Table 1. According to the energy spectrum for Mn standard compounds, in bivalent manganese oxides and bivalent manganese fluorides, the electron binding energies of Mn2p_{3/2} are 640.8 and 642.6 eV, respectively. In the pink and blue samples, the electron binding energy of Mn2p_{3/2} approximately agrees with that of bivalent manganese fluorides, indicating that Mn is in the Mn²⁺ state and mainly coordinated with F. In the green sample, the electron binding energy of Mn2p_{3/2} agrees with that of bivalent manganese oxides, indicating that Mn is in the Mn²⁺ chemical state and mainly coordinates with O. In the rose red sample, the Mn2p_{3/2} peak is asymmetric and could be decomposed into two peaks at 640.8 and 642.6 eV, consistent with those of bivalent manganese oxides and bivalent manganese fluorides, respectively, suggesting that Mn is in the Mn²⁺ chemical state and coordinates with both O and F. Also, for pink, rose red, and blue samples, Mn²⁺ occupies the Y site, whereas for the green sample it occupies the Z site in the crystal structure.

Figure 5 shows the XPS spectrum for Cr2p. Colorless, green, and rose red samples do not show the energy spectrum peak for Cr. In the blue sample, the energy spectrum peak of Cr is significantly weak, while it is relatively strong in the spectra of the pink and yellow samples. In the blue sample, the Cr2p displays a symmetric shape and situates at the position of 577.9 eV. In the pink and yellow samples, the Cr2p_{3/2} peak shows a notably asymmetric shape, which was decomposed into two peaks at 577.4 and 577.9 eV for the pink sample and at 577.5 and 578.0 eV for the yellow sample, respectively. The electron-binding energies of Cr2p_{3/2} in Cr₂O₃ and CrBO₃ are about 577.4 and 577.95 eV. Obviously, Cr in tourmaline is present in the Cr³⁺ state and coordinates with O; however, in pink and yellow samples, part of Cr also binds with O and B (Table 1). From the Cr2p_{3/2} electron-binding energies of the color tourmaline samples, it can be inferred that Cr³⁺ occupies the Z site of the crystal structure.

Pink and blue samples do not show energy peaks of Ni in the energy spectrum (Figure 6). In the colorless sample, the electron binding energy peak of Ni is extremely weak, while it is quite strong for the yellow, green, and rose red samples, which all show a good symmetric shape. The yellow and rose red samples have the same Ni2p_{3/2} electron-binding energy peak at 856.9 eV, while the green sample has the Ni2p_{3/2} peak at 853.3 eV. The Ni2p_{3/2} peak position at 856.9 eV for the yellow and rose red samples is consistent with that of the Ni standard compound Al₂NiO₄ (857.0 eV), suggesting that Ni is present in the form of Ni²⁺ and coordinates with O, and O also binds to Al in the structure [14]. Therefore, Ni clearly occupies the Y site and mainly coordinates with O in yellow and rose red samples [18]. In the green sample, the Ni2p_{3/2} electron-binding energy is 853.3 eV, in good agreement with that in

NiO, indicating that Ni in green tourmaline is present in Ni²⁺ state and is predominantly bonded to O and only occupies the Z site of the crystal structure (Table 1).

Figure 7 shows the XPS spectrum for Cu2p. Only the green sample shows a weak energy peak for Cu at 933.2 eV. The peak is generally symmetric, in good agreement with the Cu2p_{3/2} electron-binding energy (933.2 eV) in CuO. This result indicates that Cu is present in the form of Cu²⁺ and mainly coordinates with O in the green sample.

3.3. Influence of Chemical State on the Tourmaline Color. The mineral crystal color is primarily caused by the transition metal cation in the crystal composition, impurity defects, intrinsic defects, structural distortions, color centers, and charge transfer. The effects of the reflection, diffraction, and diffuse and interference of light can also result in coloration [22, 25]. In addition, a pigment ion with different coordination numbers in the crystal structure may generate different colors. For example, Co²⁺ makes minerals appear red when the coordination number is 6, whereas it makes minerals show a special blue when the coordination number is 4. It is widely believed that Fe-rich tourmaline appears dark green, dark blue, dark brown, or black. Mg-rich tourmaline appears yellow or brown. Li-rich and Mn-rich tourmaline appears rose red or light blue, and Cr-rich tourmaline is dark green [26].

The XPS results for colorless, pink, yellow, green, rose red, and blue tourmaline samples show that a color tourmaline sample usually contains various kinds of transition metal ions; however, the transition metal cations in the Y site are obviously different between the color tourmaline samples. For example, the pink sample contains Fe³⁺, Cr³⁺, and Mn²⁺, while the yellow sample contains Fe³⁺, Cr³⁺, and Ni²⁺. However, in the crystal structure, both Fe³⁺ and Cr³⁺ occupy the Z site, and Mn²⁺ and Ni²⁺ occupy the Y site. The previous investigation showed that the color of tourmaline resulted from the transition metal cations in the Y site of the structure [9]. Thus, the difference in color between the pink and yellow samples is probably dominated by the presence of Mn²⁺ or Ni²⁺ in the Y site. Although Fe³⁺, Mn²⁺, Ni²⁺, and Cu²⁺ were present in the green tourmaline sample, only Fe³⁺ occupies the Y site and coordinates with O, OH, and F, while other components Mn²⁺, Ni²⁺, and Cu²⁺ occupy the Z site and coordinate with O. Therefore, the green color of tourmaline is dominantly related to Fe³⁺ in the Y site coordinating with O, OH, and F. The rose red tourmaline sample contains Mn²⁺, Ni²⁺, and Fe³⁺, with the occupation of Fe³⁺ in the Z site and both Mn²⁺ and Ni²⁺ in the Y site in the crystal structure. Fe³⁺ coordinates primarily with O and OH, and Mn²⁺ coordinates with O and F, while Ni²⁺ binds to O. Obviously, the rose red color of tourmaline is derived from both Mn²⁺ and Ni²⁺. The blue tourmaline sample contains Fe³⁺, Mn²⁺, and Cr³⁺, but Cr³⁺ occupies the Z site and both Fe³⁺ and Mn²⁺ occupy the Y site of the crystal structure. Cr³⁺ coordinates primarily with O, Fe³⁺ coordinates with O, OH, and F, while Mn²⁺ coordinates with F. The blue color of tourmaline is derived from both Fe³⁺ and Mn²⁺ in the crystal.

According to crystal field theory, the characteristic color of many gem minerals is related to the crystal field transition

FIGURE 8: XRD spectra of tourmaline samples.

of Cr [27]. The electron configuration of Cr^{3+} is $3d^3$. Splitting the $3d^3$ electron energy level in the octahedron can lead to an energy-level transition, which is directly associated with mineral colors [25]. Furthermore, the distance between atoms directly exerts on the colors of minerals. With a long distance between Cr^{3+} and O, the splitting parameter of the octahedron crystal field is small, and thus the mineral is green; otherwise, the mineral is red. However, in the crystal structure of tourmaline, the transition metal cations related to color are located mainly in the Y site [9]. The charge transfer is the electron exchange between ions in the crystal activated by photons, which may occur between metal cations (M-M), or between O^{2-} and a metal cation. The charge transfers between O and a metal cation often involves high energy; for example, the long-wave tail in the charge transfer between O^{2-} and Fe^{3+} can occur under visible light, thus affecting color of the mineral. The peak position of the charge transfers between O and a metal cation depends on the species, coordination number, and coordination symmetry of the cation.

The color of many green silicate minerals is often associated with the peak position of the charge transfer between O^{2-} and Fe^{3+} . The charge transfer between transition metal cations often occurs between coedge or coplanar coordination octahedrons; however, the color-induced transition metal cations occupy the same Y site in the structure and charge transfer between metal cations (M-M) is not expected [28].

The XRD results are shown in Figure 8. The sharp peaks of all the tourmaline samples show that all samples are generally well crystallized; however, the colorless tourmaline sample with no detected trace elements in the structure displays the most intensive reflections compared to other samples especially for the weak peaks in the patterns, suggesting that the colorless sample has the most well-crystallized crystal and ordered structure [29]. On the contrary, the colorful tourmaline samples with certain amounts of trace elements show relatively lower peak intensity and/or different peak ratios of characteristic reflections, indicating the presence of impurity defects and structural distortion in the crystals due to the

substitutions of trace elements. Therefore, differences in the chemical environment, including the types of coordination anions, impurity defects, and structural distortion, can lead to different electronic transitions, which may also be the reason for color differences in tourmaline.

4. Conclusions

A color tourmaline sample usually contains several species of transition metal elements. However, there is distinctive difference in element of the transition metals in the Y site between different color samples. The pink color of tourmaline is caused by Mn^{2+} occupying the Y site of the crystal structure, while green is attributed to Fe^{3+} occupying the Y site. The yellow color of tourmaline is related to Ni^{2+} bonding primarily with O, while rose red is derived from both Mn^{2+} and Ni^{2+} in the Y site. The blue color is attributed to Fe^{3+} and Mn^{2+} in the Y site. The charge transfer between cation pairs is unlikely to take place in the color-induced cations of the sole Y site, and the color of tourmaline is probably induced from the absorption of the d-d transition of transition metals in the crystal structure instead.

Conflicts of Interest

The authors declare that there is no conflict of interest with any institution or funding body.

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