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Classification of natural tourmalines using near-infrared absorption spectroscopy

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Abstract. Six natural tourmaline crystals with different colors were investigated by near-infrared (NIR) absorption spectroscopy. The tourmaline crystals were obtained from Lucyen mines in Vietnam. The NIR absorption spectra were recorded in two ranges of 4000-5000 cm^{-1} and 6500-8000 cm^{-1}. We found, according to their NIR spectra features, these six tourmaline crystals can be classified into four groups: G1, liddicoatite; G2, elbaite; G3, dravite; and G4, Uvite. This grouping is consistent with the chemical composition analyses and our earlier Raman studies.

Keywords: Tourmaline, NIR absorption, OH vibration.

1. Introduction

Tourmaline is rock-forming mineral which has been found in various regions over the world, including Lucyen mines in Vietnam. Tourmaline consists of important information related to the mineralogical and metallogenic history of the rock. Therefore, the study of tourmaline physical properties is helpful to understand the geological formation of the area where the tourmaline is located [1]. Tourmaline has a complex chemical composition with a general formula of $XY_3Z_6(T_6O_{18})(BO_3)_3V_3W$. The X-sites are occupied by Na^+ and Ca^{2+}, or Mg^{2+}, Fe^{2+} and Mn^{2+} cations. The Y-sites are occupied by ions such as Li^+, Mg^{2+}, Fe^{2+}, Mn^{2+}, Al^{3+}, Fe^{3+}, Mn^{3+}, Cr^{3+}. The Z-sites are generally substituted by Al^{3+} cations, sometime by different cations such as Fe^{2+}, Mg^{2+}, Li^+, Cr^{3+}, V^{3+}, etc. The T-sites are typically occupied by Si, but a mall number of B and Al elements may be found in these sites [2,3]. Anions, such as O^{2-} and OH^- can occupy the V-sites, while O^{2-}, OH^-, and F^- can occupy the W-sites. Normally, tourmalines are classified based on the different ions occupied in the Y and Z sites. According to the International Mineral Association (IMA), there are fourteen kinds of tourmalines: elbaite, schorl, dravite, olenite, chromdravite, buergerite, povondraite, vanadiumdravite, liddicoatite, uvite, feruvite, rossmanite, foitite, and magnesiofoitite.

The OH groups in tourmaline can occupy two sites, i.e., OH_1 groups on W-sites and OH_3 groups on V sites. The OH_1 group connects with three Y cations, while the OH_3 group relates with two Z cations and one Y cation. The occupation of Y and Z sites by different cations would influence the

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frequencies of the OH vibrations [4,5]. Thus, the study of OH vibrations would be helpful to achieve important information about the Y and Z metal cations in tourmalines.

Crystal vibrations of tourmalines have been investigated by Raman scattering spectroscopy [6-10] and infrared (IR) spectroscopy [1, 4, 11-13]. The Raman studies have been mainly focused on the vibrations of cation bonds. In our earlier Raman study [14], we reported the OH vibrations in the range of 3000 – 4000 cm^{-1}, and we showed that tourmalines can be easily classified according to their Raman features of OH vibrations in this spectral range. The earlier IR studies were mainly focused on the OH vibrations in the spectral ranges of 3750-3630 cm^{-1}, 3600-3400 cm^{-1} and 3400-3200 cm^{-1} [4, 11-13]. In the study of Frost et al [1], a wide absorption region from infrared to visible was reported on two Mn rich tourmalines. In this paper, we present the near infrared absorption in the spectral regions of 4000-5000 cm^{-1} and 6500-8000 cm^{-1} for six natural tourmaline crystals with different colors. We show that according to their NIR spectra features, these six tourmaline crystals can be classified into four groups: G1, liddicoatite; G2, elbaite; G3, dravite; and G4, Uvite. This grouping is consistent with the chemical composition analyses and our earlier Raman study.

2. Experimental

Six natural tourmaline crystals with different colors were used in our study. These tourmalines were obtained from the Lucyen mines in Vietnam. Phase identification of these tourmalines was verified by powder X-ray diffraction (XRD, Siemen D5005). Chemical composition identification of these tourmalines was verified by Energy dispersive X-ray ***spectroscopy*** (EDXS, Hitachi 4500 SEM). The results of the detailed analysis of the XRD and EDXS studies are presented in Table 1.

For the NIR absorption study, the tourmaline crystals were cut perpendicularly with C axis and polished two faces. The NIR spectra were performed on Jasco V-670 spectrophotometer. The NIR spectrum was obtained from 10,000 to 4000 cm^{-1} at the resolution of 4 cm^{-1}.

3. Results and discussion

3.1. The chemical composition of tourmaline

In previous paper [14], we presented the results of phase structure and chemical composition studies. Base on the molar ratio of each composition, six tourmaline samples were classified into four groups: G1, liddicoatite; G2, elbaite; G3, dravite; and G4, Uvite (Table 1).

Table 1. Average composition (wt%) analyses and types assignments of tourmalines.

Sample	G1	G2	G3	G4		
Element	X1	X2	X3	X4	X5: green	X6: brown
B (calculated)	6.23	11.28	7,64	12.35	10.28	9.83
O	55.33	57.51	55,83	56.00	53.73	57.84
Na	0.62	1.06	-	1.60	1.70	1.43
Mg	-	-	6,64	5.74	5.48	5.68
Al	17.92	17.47	13,20	12.56	13.95	11.80
Si	13.27	11.62	13,17	11.54	12.62	10.66
Ca	2.37	0.86	1,00	0.21	0.53	2.15
Fe	-	0.20	-		0.62	-
F	3.23	-	-	-	-	-
Li	1.02	-	-	-	-	-
V	-	-	0,74	-	-	-
Cr	-	-	0,56	-	-	-
Ce	-	-	1,21	-	-	-
Ba	-	-	-	-	-	0.62
Types	liddicoatite	elbaite	davite	uvite		
Chemical composition	(Ca,Na) (Li,Al)3 (Al)6 (BO3)3 Si6O18 (O,OH,F)4	(Na,Ca) (Fe,Al)3 (Al)6 (BO3)3 Si6O18 (OH)4	(Ca) (Mg)3 (Al) 6 (BO 3)3 Si6O18 (OH)4	(Na,Ca) (Mg, Fe)3 Al5Mg (BO3)3 Si6O18 (OH)4	(Na,Ca) (Mg)3 Al5Mg (BO3)3 Si6O18 (OH)4	(Ca,Na) (Mg,Ba)3 Al5Mg (BO3)3 Si6O18 (OH)4

3.2. The classification of tourmaline based on the NIR spectra related to OH group vibrations

Figure 1a shows the NIR absorption spectrum of X1 tourmaline in the range of 4000-5000 cm^{-1}. The vibrations in this spectral range would be correlated to the combination of the stretching and bending modes of cationic hydroxyl M-OH units (M may be Al, Fe, Mg, etc.). The intense band at 4597 cm^{-1} can be assigned to Al(OH$_1$) vibrations, where OH$_1$ connects with three cations Al^{3+} in Y-sites. The band at 4537 cm^{-1} can be assigned to the combination of Al-OH$_1$ bending and O-H$_1$ stretching mode in Al(Y)Al(Y)Li(Y) environment. The band at 4447 cm^{-1} can be attributed to the combination of stretching and bending modes of Li(OH$_1$) units in Al(Y)Al(Y)Li(Y) environment based on the substitution of Li in Y-sites. Three bands located at 4346 cm^{-1}, 4152 cm^{-1} and 4051 cm^{-1} might be due to the combination of stretching and bending mode of M-OH$_3$, where 4346 cm^{-1} and 4152 cm^{-1} bands gradually relate to Al(OH$_3$) in Al(Z)Al(Z)Al(Y) and Al(Z)Al(Z)Li(Y) environments, and 4051 cm^{-1} band relates to Li(OH$_3$) in Al(Z)Al(Z)Li(Y) environment.

Figure 1b shows the NIR absorption spectra of X1 tourmaline in the range of 6500-8000 cm^{-1}. This range would cover the overtone of OH stretching mode [1]. The presence of 7581 cm^{-1} absorption band in X1 samples can be attributed to the combination of the overtone of OH$_1$ stretching in Al(Y)Al(Y)Al(Y) environment and Al-OH$_1$ bending mode due to the major occupation of Al into Y-sites in liddicoatite. The shoulder at the higher wavenumber 7648 cm^{-1} can be assigned to the presence of Li in Y-site. The two bands at 7127 cm^{-1} and 7030 cm^{-1} are assigned to the first overtone of OH$_1$

groups in Al(Y)Al(Y)Al(Y) and Al(Y)Al(Y)Li(Y) environment. The two bands at 6823 cm^{-1} and 6733 cm^{-1} are attributed to the first overtone of OH$_3$ groups related to two cations Al^{3+} in Z-sites and one cation Al^{+} or Li^{3+} in Y-sites.

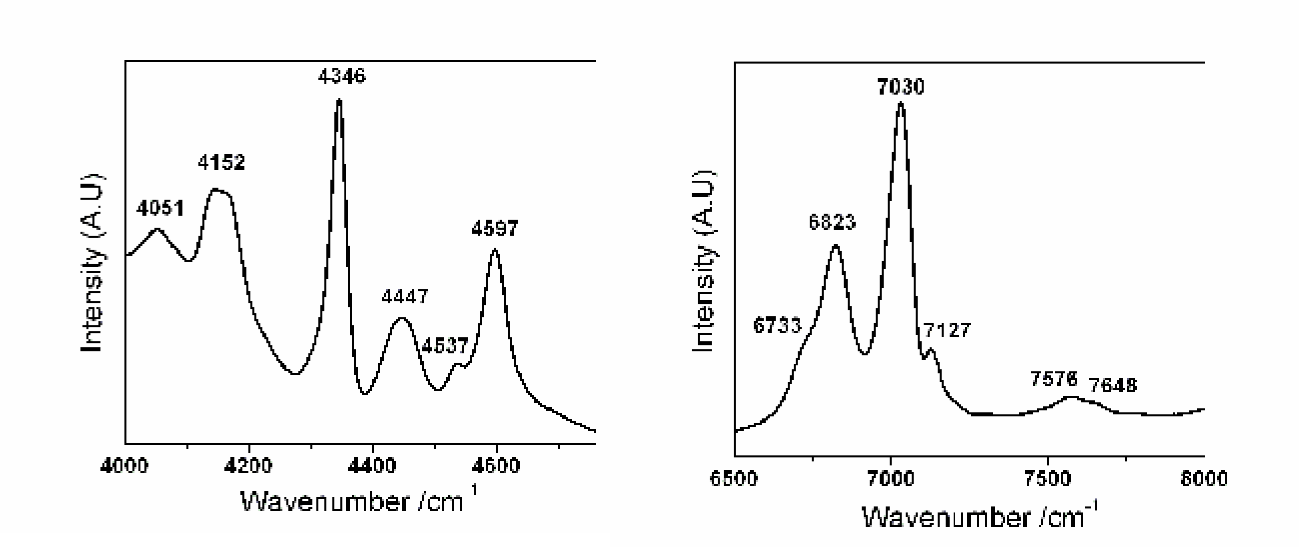

Fig. 1. The NIR spectra of liddicoatite(X1) in (a) 4000-5000 cm^{-1} and (b) 6500-8000 cm^{-1} regions.

To investigate the influence of the occupation of Y and Z sites by various metal cations to the vibration frequencies of OH group in tourmaline, we present the absorption spectra related to OH group of six tourmaline samples in the same coordinate (figure 2). Figure 2a and 2b gradually depict the NIR absorption spectra originated from the combination of O-H stretching and M-OH bending modes and the first overtone of O-H stretching mode in which M can be Al, Mg, Fe, Li, etc. Based on the individual absorption features of each sample as shown in figure 2, six tourmaline samples can be classified into four groups: G1, liddicoatite; G2, elbaite; G3, dravite; and G4, Uvite which agrees with the result achieved from EDXS analysis.

For elbaite (X2), the 4438 cm^{-1} band replaces the 4447 cm^{-1} band in liddicoatite (X1) due to the replacement of Fe for Li element in Y-sites. Therefore, the 4438 cm^{-1} band can be assigned to the combination of stretching and bending modes of Fe(OH$_1$) units in Al(Y)Al(Y)Fe(Y) environment. Similarly, the 4018 cm^{-1} and 4157 cm^{-1} bands gradually replace the 4051 cm^{-1} and 4152 cm^{-1} bands in liddicoatite due to the presence of Fe element in Y-sites. In 6500-8000 cm^{-1} region, the replacement of Fe for Li element in Y-sites of elbaite also makes a difference between the 7009 cm^{-1} band and 7030 cm^{-1} band. The 7009 cm^{-1} band can be assigned to the first overtone of OH$_1$ stretching vibration in Al(Y)Al(Y)Fe(Y) environment. The 6784 cm^{-1} band actually includes two sub-bands related to the first overtone of OH$_3$ group in which one band at 6823 cm^{-1} is similar with that in liddicoatite and the another band at the lower wavenumber is due to OH$_3$ vibration in Al(Z)Al(Z)Fe(Y) environment.

Different from liddicoatite and elbaite, the Y-sites in dravite (X3) are completely occupied by Mg element. Therefore, instead of the 7581 cm^{-1} band in liddicoatite, the 7657 cm^{-1} band appears in dravite (figure 2b) which is attributed to the combination of the first overtone of OH$_1$ stretching in

Mg(Y)Mg(Y)Mg(Y) environment and Mg-OH_1 bending mode. The 7302 cm^{-1} and 6992 cm^{-1} bands gradually correspond to the first overtone of OH_1 stretching mode related to three Mg^{2+} cations in Y sites and the first overtone of OH_3 stretching mode in Al(Z)Al(Z)Mg(Y) environment. In the lower wavenumber region (figure 2a), the 4457 cm^{-1} band of dravite is assigned to the combination of OH_1 stretching in Mg(Y)Mg(Y)Mg(Y) environment and Mg-OH_1 bending mode. The 4249 cm^{-1} band is attributed to the combination of OH_3 stretching in Al(Z)Al(Z)Mg(Y) environment and Al-OH_3 bending mode. The appearance of the 7361 cm^{-1} and 7085 cm^{-1} bands in the 6500-8000 cm^{-1} region and the 4513 cm^{-1} band in the 4000-5000 cm^{-1} region may be due to small number of dopants in Y and Z sites.

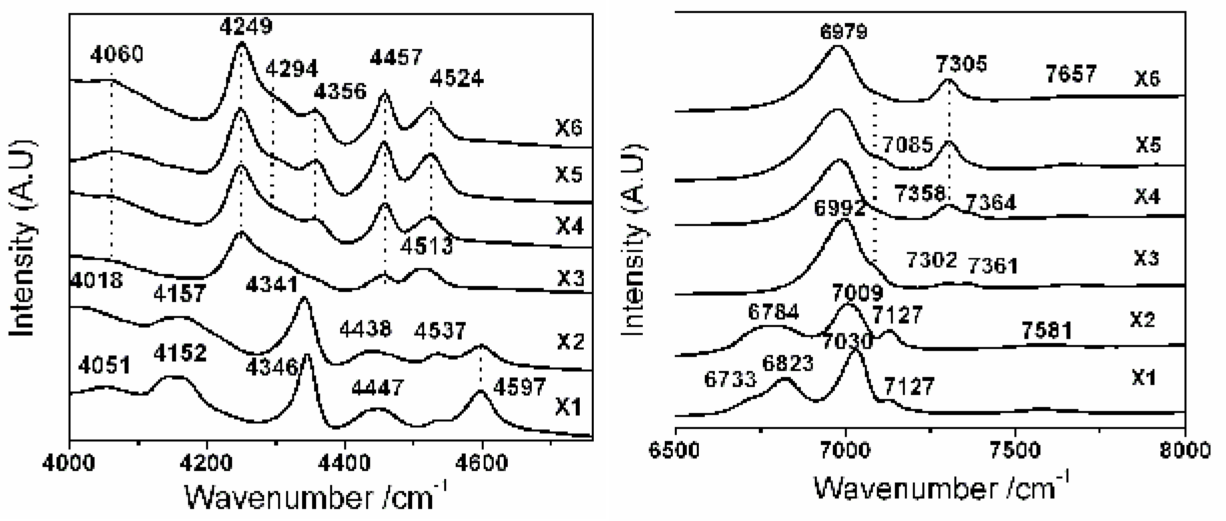

Fig. 2. The NIR spectra of different tourmaline samples in (a) 4000-5000 cm^{-1} and (b) 6500-8000 cm^{-1} regions.

It can be seen from Fig. 2 that, the absorption features of uvite (X4, X5 and X6) are similar with that of dravite (X3). However, the 6992 cm^{-1} band is replaced by the 6979 cm^{-1} band which is asymmetric for three uvite samples. This structure actually includes another band at lower wavenumber which can be attributed to the first overtone of OH_3 stretching mode in Al(Z)Mg(Z)Mg(Y) environment due to the presence of Mg element in Z-sites. In addition, due to the small number of Fe and Ba elements in Y-sites, the absorption spectra of uvite appear two bands near 7364 cm^{-1} and 7085 cm^{-1} which gradually can be related to the vibration of OH_1 group connected with two cations Mg^{2+} and one cation Ba^{2+} or Fe^{2+} in Y-sites and the vibration of OH_3 group in Al(Z)Al(Z)Fe(Y) or Al(Z)Al(Z)Ba(Y) environments. In the lower wavenumber region, the 4524 cm^{-1} band can be originated from the combination of OH_1 stretching in Mg(Y)Mg(Y)Ba(Y) or Mg(Y)Mg(Y)Fe(Y) environment and Mg-OH_1 bending mode due to the presence of Ba or Fe in the Y-sites. The 4356 cm^{-1} band is assigned to the combination of O-H_3 stretching in the Al(Z)Al(Z)Mg(Y) environment and Mg-OH_3 bending mode while the 4294 cm^{-1} band is attributed to the combination of OH_3 stretching in the Al(Z)Al(Z)Fe(Y) or Al(Z)Al(Z)Ba(Y) environment and Al-OH_3 bending mode. A weak band at 4060 cm^{-1} may be attributed to OH_3 stretching mode in Al(Z)Al(Z)Fe(Y) or Al(Z)Al(Z)Ba(Y) environment combined with Fe-OH_3 or Ba-OH_3 bending mode (similar with the 4051 cm^{-1} band in liddicoatite).

4. Conclusion

In summary, the occupation of Y and Z sites by various metal cations influences noticeably on vibration frequencies of OH groups and induces the individual absorption features for each tourmaline sample. The absorption spectra of tourmaline related to OH group vibrations presents in two regions which are 4000-5000 cm^{-1} and 6500-8000 cm^{-1}. The 6500-8000 cm^{-1} absorption region is explained due to the first overtone of OH stretching mode while the 4000-5000 cm^{-1} one originates from the combination of the OH stretching and M-OH bending mode. Based on the absorption features in both regions, the tourmalines were classified into four groups and the grouping characterizations are consistent with the chemical compositions results.

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