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DISORDERED Mg-BEARING OLENITE FROM A GRANITIC PEGMATITE AT GOSLARN, AUSTRIA: A CHEMICAL, STRUCTURAL, AND INFRARED SPECTROSCOPIC STUDY

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ABSTRACT

The core and rim of a short prismatic dark brown tourmaline crystal (10 mm in diameter) from a granitic pegmatite near Goslarn, Lower Austria, were structurally and chemically characterized, including H_2O determination and Mössbauer analysis. The optimized formula, calculated using chemical and structural data for the core, is ${}^{X}(Na_{0.64}Ca_{0.11}K_{002}\square_{0.23})$ ${}^{Y}(Al_{1.58}Mg_{0.91}Fe^{2+}{}_{0.41}Ti_{0.10})$ ${}^{Z}(Al_{4.90}Mg_{1.10})$ ${}^{T}(Si_{6.00})$ B_3O_{27} $[(OH)_{3.07}O_{0.90}F_{0.03}]$, with a 15.9149(3), c 7.1757(2) Å, $R = 0.014$. The optimized formula for the rim is ${}^{X}(Na_{0.71}Ca_{0.10}K_{001}\square_{0.18})$ ${}^{Y}(Al_{1.42}Mg_{1.10}Fe^{2+}{}_{0.39}Ti_{0.09})$ ${}^{Z}(Al_{4.94}Mg_{1.06})$ ${}^{T}(Si_{5.95}Al_{0.05})$ B_3O_{27} $[(OH)_{3.05}O_{0.92}F_{0.03}]$, with a 15.9238(4), c 7.1822(2) Å, $R = 0.014$. Mg and Al are highly disordered in this sample of tourmaline, and the O1 site is occupied by $\sim[O_{0.9}(OH)_{0.1}]$. Such samples of magnesian olenite provide a very good example of disorder driven by the short-range requirements of O^{2-} at the O1 site that is associated with the ~2Al + Mg configuration at the coordinating Y sites. To date, these tourmaline samples have the highest Al content at the Y site (up to ~1.6 *apfu*) for Mg-rich tourmaline. Three quadrupole-splitting distributions were used to represent the contributions of Y-site Fe^{2+} in the Mössbauer spectrum. The absence of Fe^{3+} reflects the low fugacity of oxygen in this pegmatite. The infrared (IR) spectrum shows four bands. These bands, at ~4528, 4457, 4358 and 4241 cm^{-1}, are combinations of OH stretching + MOH bending motions. In the fundamental OH region, only three bands at ~3737, 3630 (sh) and 3552 cm^{-1} are clearly observed. The relatively sharp bands and the very low R-values of the crystal-structure refinements indicate a high degree of crystallinity. The strong band at ~3552 cm^{-1} can be assigned to O–H3 stretching, which is in agreement with an occupancy of $\sim(OH)_3$ at the V site. The band at ~3630 cm^{-1}, which can be assigned to O–H1 stretching, is relatively small. This is in agreement with the occupancy of $\sim[O_{0.9}(OH)_{0.1}]$ at the W site. We assess the assignment of Mg-rich tourmaline to dravite or olenite, and different methods to approximate the Al–Mg order, where there is no possibility for a single-crystal determination of the structure.

Keywords: tourmaline, olenite, crystal structure, chemical analyses, infrared spectroscopy, Goslarn, Austria.

SOMMAIRE

Nous avons caractérisé la structure et la composition du coeur et de la bordure d'une variété de tourmaline brune se présentant en prismes trappus (10 mm de diamètre) dans une pegmatite granitique près de Goslarn, en Basse Autriche; nous avons aussi déterminé la teneur en H_2O et le spectre de Mössbauer. La formule optimisée, calculée à partir des données chimiques et structurales pour le coeur, est ${}^{X}(Na_{0.64}Ca_{0.11}K_{002}\square_{0.23})$ ${}^{Y}(Al_{1.58}Mg_{0.91}Fe^{2+}{}_{0.41}Ti_{0.10})$ ${}^{Z}(Al_{4.90}Mg_{1.10})$ ${}^{T}(Si_{6.00})$ B_3O_{27} $[(OH)_{3.07}O_{0.90}F_{0.03}]$, avec a 15.9149(3), c 7.1757(2) Å, $R = 0.014$. La formule optimisée pour la bordure du cristal est

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$^{X}(Na_{0.71}Ca_{0.10}K_{001}\square_{0.18})$ $^{Y}(Al_{1.42}Mg_{1.10}Fe^{2+}{}_{0.39}Ti_{0.09})$ $^{Z}(Al_{4.94}Mg_{1.06})$ $^{T}(Si_{5.95}Al_{0.05})$ B_3O_{27} $[(OH)_{3.05}O_{0.92}F_{0.03}]$, avec *a* 15.9238(4), *c* 7.1822(2) Å, *R* = 0.014. Le magnésium et l'aluminium sont fortement désordonnés dans cet échantillon, et le site O1 site est peuplé par ~$[O_{0.9}(OH)_{0.1}]$. De tels cristaux d'olénite magnésienne fournissent un bon exemple de désordre causé par les exigeances à courte échelle de O^{2-} occupant le site O1 en association avec l'agencement ~2Al + Mg aux sites *Y* avoisinants. Ces échantillons de tourmaline font preuve de la teneur en Al la plus élevée au site *Y* (jusqu'à ~1.6 atomes par unité formulaire) pour une tourmaline magnésienne. Trois distributions de l'écartement quadrupolaire ont été utilisées pour représenter les contributions de Fe^{2+} au site *Y* dans le spectre de Mössbauer. L'absence de Fe^{3+} témoigne de la faible fugacité d'oxygène dans cette pegmatite. Le spectre infrarouge (IR) contient quatre bandes. Ces bandes, à ~4528, 4457, 4358 et 4241 cm^{-1}, résultent d'une combinaison de l'étirement OH et des mouvements de flexure dans l'agencement *M*OH. Dans la région fondamentale de l'hydroxyle, seulement trois bandes, à ~3737, 3630 (fine) et 3552 cm^{-1}, sont clairement observées. La présence de bandes relativement fines et les valeurs très faibles de *R* dans les affinements de la structure indiquent un niveau élevé de cristallinité. On peut attribuer la bande intense à ~3552 cm^{-1} à l'étirement O–H3, ce qui concorde avec une occupation du site *V* par ~$(OH)_3$. La bande à ~3630 cm^{-1}, que l'on peut attribuer à l'étirement O–H1, est relativement faible, ce qui concorde avec la présence de ~$[O_{0.9}(OH)_{0.1}]$ au site *W*. Nous évaluons l'attribution de cette tourmaline magnésienne à la dravite ou à l'olénite, et les diverses méthodes d'en évaluer le degré d'ordre là où il n'y a aucune possibilité d'effectuer une détermination de la structure d'un monocristal.

(Traduit par la Rédaction)

Mots-clés: tourmaline, olénite, structure cristalline, analyses chimiques, spectroscopie infrarouge, Goslarn, Autriche.

INTRODUCTION

Hawthorne & Henry (1999) gave the general chemical formula of the tourmaline-group minerals as $X\,Y_3\,Z_6$ $[T_6O_{18}]$ $(BO_3)_3$ V_3 W [*V* site: O3 site, *W* site: O1 site]. The *Z* site can be occupied by Al, Mg, Fe^{3+}, V^{3+} and Cr^{3+}. The substitution of Al for Mg at the *Z* site was described by Grice & Ercit (1993), Hawthorne *et al.* (1993), MacDonald & Hawthorne (1995), Taylor *et al.* (1995), Bloodaxe *et al.* (1999), and Cámara *et al.* (2002). Hawthorne *et al.* (1993) asserted that the Mg content at the *Z* site cannot be determined on the basis of scattering power alone because of the similarity of Mg and Al with respect to X-ray scattering. Because of considerable differences in ionic radius between Al and Mg, their quantity can be determined from mean bond-lengths. Hawthorne *et al.* (1993) and Grice & Ercit (1993) obtained linear relations between mean bond-lengths and the radii of constituent cations. After normalizing the *Y*-site and *Z*-site constituents to nine cations before the final refinement, Bloodaxe *et al.* (1999) used the method of Hawthorne *et al.* (1993) to determine the extent of order of Mg and Al between the two octahedral sites by minimizing the differences between grand mean octahedral bond-length and bond lengths calculated from the radii of the constituent cations. The final assignments in Bloodaxe *et al.* (1999) were made by minimizing the difference between the error on *Y* and *Z*.

Ertl (1995) gave unit-cell parameters and results of semiquantitative analyses of light brown to dark brown Mg-rich tourmaline from small veins of pegmatite in a gneiss (paragneiss of the Bunte Serie of the Gföhler unit) near the village of Goslarn, Lower Austria. These tourmaline crystals are short, prismatic, and reach up to 1 cm in diameter. The associated minerals are quartz, apatite, sillimanite and microcline. We initiated this investigation because of the unusual (for tourmaline from a granitic pegmatite) short prismatic habit of these crystals, and the relatively low Fe content (Ertl 1995). Here, we provide results of detailed analyses of a tourmaline crystal (Mg-bearing olenite) from that pegmatite, giving chemical, structural, Mössbauer analytical data, and infrared spectroscopic data for the material, and we also discuss the degree of order of Mg over the *Y* and *Z* sites.

EXPERIMENTAL

Sample selection

Pieces from the rim (*GOS1*) and from the core (*GOS2*) were separated from a dark brown short prismatic tourmaline crystal (10 mm in diameter, 7 mm in length) from Goslarn, Lower Austria. This euhedral crystal is intergrown with quartz and shows the forms {101}, {120} and {010}. The two pieces were first used for structure refinements and subsequently for chemical analysis.

Crystal structure

Crystals *GOS1* (~150 μm in diameter) and *GOS2* (~200 μm in diameter) were mounted on a Bruker Apex CCD diffractometer employing graphite-monochromated Mo*K*α radiation. Redundant data were collected for an approximate sphere of reciprocal space, and were integrated and corrected for Lorentz and polarization factors using the Bruker program SaintPlus (Bruker AXS Inc. 2001).

The structures were refined using the Bruker SHELXTL v. 6.10 package of programs, with neutral-atom scattering factors and terms for anomalous dispersion. Refinement was done with anisotropic thermal parameters for all non-hydrogen atoms. Table 1 lists crystal data and details of structure refinement for the two tourmalines. Table 2 contains the atom coordinates, equivalent-isotropic displacement parameters, and site occupancies. Table 3 shows selected bond-lengths. Structure factors may be obtained from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

Chemical analysis

The two single crystals used for the structure refinement were analyzed with a wavelength-dispersion ARL SEMQ electron microprobe (EMP) at the Naturhistorisches Museum Wien, Austria (Table 4). We used an accelerating voltage of 15 kV, a beam current of 15 nA, and a spot size of 2 μm. Natural silicates and oxides were used as standards. The concentration of fluorine was determined by F-ion sensitive electrodes on a bulk sample from which our two crystals were obtained. The bulk sample of the tourmaline crystal was further analyzed for H content in the Stable Isotope Laboratory at Southern Methodist University (U extraction method; Dyar *et al.* 1998).

The amount of B_2O_3 was calculated as B = 3.00 *apfu* by assuming that there is no $^{[4]}$B in this sample of tourmaline; this assumption is supported by the structure refinements and also the <*T*–O> distances of 1.619–1.620 Å (Table 3). The ideal <*T*–O> bond length (*T* site fully occupied with Si) has been determined to be ~1.620 Å in various structural studies (MacDonald & Hawthorne 1995, Bloodaxe *et al.* 1999, Ertl *et al.* 2001a).

Mössbauer analysis

Approximately 80 mg of tourmaline was crushed to a fine powder with sugar under acetone before mounting in a sample holder confined by cello tape. The resultant thickness of the sample was 0.44 mg Fe/cm^2, below the approximation of thin-absorber thickness (Long *et al.* 1983). A room-temperature Mössbauer spectrum to determine Fe^{2+} and Fe^{3+} content was acquired in the Mineral Spectroscopy Laboratory at Mount Holyoke College (Fig. 1). A source of 20 mCi ^{57}Co in Rh was used on a WEB Research Co. spectrometer; run time was ten days. Results were calibrated against an α-Fe foil of 6 μm thickness and 99% purity. In the

TABLE 1. CRYSTAL DATA AND DETAILS OF STRUCTURE REFINEMENTS OF OLENITE FROM GOSLARN, LOWER AUSTRIA

Space group: *R*3*m*		
Unit-cell parameters (Å):		
	GOS1: *a* 15.9238(4), *c* 7.1822(2)	*GOS2*: *a* 15.9149(3), *c* 7.1757(2)
Frame width, scan time, number of frames, detector distance: 0.20°, 15 s, 4500, 5 cm		
Measured reflections, full sphere:		
	GOS1: 11,613	*GOS2*: 36,596
Unique reflections; refined parameters:		
	GOS1: 1,125; 93	*GOS2*: 1,127; 93
*R*1, $I > 4\sigma_I$:		
	GOS1: 0.0143	*GOS2*: 0.0137
Difference peaks (+,–):		
	GOS1: 0.29, 0.20	*GOS2*: 0.23, 0.19
Goodness-of-fit:		
	GOS1: 1.079	*GOS2*: 1.098

TABLE 2. ATOM POSITIONS AND EQUIVALENT ISOTROPIC *U* VALUES IN OLENITE FROM GOSLARN, LOWER AUSTRIA

Atom	*x*	*y*	*z*	U_{eq}	Occup.
			GOS1		
Na	0	0	3/4	0.02078(10)	0.908(1)
Si	0.808262(5)	0.810184(6)	0.978909(17)	0.00682(2)	1.00
B	0.890153(19)	0.78031(4)	0.52491(7)	0.00852(10)	3.00
^{Y}Al	0.876224(10)	0.938112(5)	0.34550(2)	0.01107(3)	1.139(1)
^{Z}Al	0.702205(6)	0.738561(6)	0.368213(17)	0.00745(2)	0.995(1)
O1	0	0	0.20634(9)	0.01565(14)	1.00
O2	0.939088(13)	0.87818(3)	0.49222(5)	0.01398(8)	1.00
O3	0.73740(3)	0.868699(16)	0.46854(5)	0.01517(8)	1.00
O4	0.906579(14)	0.81316(3)	0.90805(5)	0.01235(7)	1.00
O5	0.81520(3)	0.907599(14)	0.88624(5)	0.01260(7)	1.00
O6	0.804646(15)	0.814916(16)	0.20231(4)	0.01067(6)	1.00
O7	0.714675(16)	0.714836(15)	0.90080(3)	0.01027(6)	1.00
O8	0.790650(16)	0.729803(16)	0.53925(4)	0.01139(6)	1.00
H3	0.7391(7)	0.8695(3)	0.5862(13)	0.043(3)	1.00
			GOS2		
Na	0	0	3/4	0.02086(11)	0.883(1)
Si	0.808301(5)	0.810218(6)	0.977247(17)	0.00705(2)	1.00
B	0.89020(2)	0.78039(4)	0.52361(7)	0.00889(10)	3.00
^{Y}Al	0.876540(10)	0.938270(5)	1.34333(2)	0.01095(3)	1.159(1)
^{Z}Al	0.702229(6)	0.738604(7)	1.366903(18)	0.00768(2)	0.996(1)
O1	0	0	1.20486(10)	0.01615(14)	1.00
O2	0.939142(14)	0.87828(3)	0.49029(6)	0.01410(8)	1.00
O3	0.73798(3)	0.868991(16)	1.46729(5)	0.01588(8)	1.00
O4	0.906525(15)	0.81305(3)	0.90640(5)	0.01258(8)	1.00
O5	0.81492(3)	0.907462(15)	0.88442(5)	0.01288(8)	1.00
O6	0.804886(16)	0.815142(17)	1.20088(4)	0.01099(6)	1.00
O7	0.714600(17)	0.714794(16)	0.89954(4)	0.01051(6)	1.00
O8	0.790756(17)	0.729849(17)	0.53808(4)	0.01183(6)	1.00
H3	0.7405(7)	0.8703(4)	0.5831(14)	0.044(3)	1.00

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) IN OLENITE FROM GOSLARN, LOWER AUSTRIA

		GOS1	***GOS2***			***GOS1***	***GOS2***
X-	O2 (x3)	2.5001(4)	2.5074(4)	*T*-	O7	1.6057(2)	1.6051(2)
	O5 (x3)	2.7299(4)	2.7271(4)		O6	1.6087(3)	1.6088(3)
	O4 (x3)	2.8156(4)	2.8105(4)		O4	1.6242(2)	1.6229(2)
Mean		2.682	2.682		O5	1.6402(2)	1.6392(2)
				Mean		1.620	1.619
Y-	O2 (x2)	1.9947(3)	1.9918(3)				
	O6 (x2)	1.9923(3)	1.9876(3)	B-	O2	1.3699(6)	1.3702(7)
	O1	1.9780(4)	1.9705(4)		O8 (x2)	1.3761(3)	1.3745(4)
	O3	2.1086(4)	2.1067(5)	Mean		1.374	1.373
Mean		2.010	2.006				
Z-	O6	1.8910(2)	1.8927(3)				
	O8	1.8926(2)	1.8917(3)				
	O7	1.9005(3)	1.8995(3)				
	O8'	1.9257(3)	1.9260(3)				
	O7'	1.9530(2)	1.9512(2)				
	O3	1.9916(2)	1.9920(1)				
Mean		1.926	1.926	GOS1: rim		GOS2: core	

absence of any data on recoil-free fractions for Fe at different sites and for valences in the tourmaline structure, peak areas were assumed to correspond directly to the abundance of the species in the sample; it is recognized that this assumption (and the use of a potentially preferentially oriented absorber) may unavoidably contribute to the overall large errors on the Fe distributions in this sample. Thus, the error on site assignments in this sample is estimated to be roughly ±3–5%.

The spectrum was fit using the WMOSS software of WEB Research Co., an implementation of the Voigt-based method of fitting the spectrum developed by Rancourt & Ping (1991). This method has been shown to be most appropriate for samples in which the Fe atoms do not have homogeneous environments, but rather have different nearest-neighbor and next-nearest-neighbor environments. This is certainly the case in the tourmaline structure. Given the poor signal-to-noise ratio of the spectrum (a result of the sample's relative low Fe content), elaborate schemes of fitting were not considered. Instead, a simple three-doublet fit was used. Various combinations of constraints for the parameters of each distribution were used, but these permutations did not affect the relative peak-areas by more than ±3% (*i.e.,* within the stated error).

TABLE 4. CHEMICAL COMPOSITION OF TOURMALINE FROM GOSLARN, LOWER AUSTRIA

	GOS1 (rim)[1]	*GOS1* (rim)[2]	*GOS2* (core)[1]	*GOS2* (core)[2]
SiO_2 wt.%	36.54	36.92	36.75	37.22
TiO_2	0.87	0.74	0.98	0.82
B_2O_3	10.68[3]	10.79	10.70[3]	10.78
Al_2O_3	33.55	33.75	34.03	34.11
FeO	3.05	3.04	3.32	3.04
MgO	8.87	8.99	8.54	8.36
CaO	0.53	0.58	0.63	0.64
Na_2O	2.00	2.27	2.00	2.05
K_2O	0.03	0.05	0.05	0.10
F	0.05[4]	0.06	0.05[4]	0.06
H_2O	2.85[5]	2.84	2.85[5]	2.85
O=F	-0.02	-0.03	-0.02	-0.03
Sum	98.93	100.00	99.88	100.00
Si *apfu*	5.99	5.95	5.98	6.00
$^{[4]}Al$	0.01	0.05	0.02	0.00
Sum *T* site	6.00	6.00	6.00	6.00
$^{[3]}B$	3.00	3.00	3.00	3.00
Al	6.48	6.36	6.52	6.48
Mg	2.17	2.16	2.07	2.01
Ti	0.11	0.09	0.12	0.10
Fe^{2+}	0.42	0.39	0.45	0.41
Sum *Y*, *Z* sites	9.18	9.00	9.16	9.00
Ca	0.09	0.10	0.11	0.11
Na	0.64	0.71	0.63	0.64
K	0.01	0.01	0.01	0.02
Sum *X* site	0.74	0.82	0.75	0.77
Sum cations	18.92	18.82	18.91	18.77
H	3.12	3.05	3.09	3.07
F	0.03	0.03	0.03	0.03
Sum OH + F	3.15	3.08	3.12	3.10

[1] Average result of five EMP analyses. [2] Wt. percent calculated from optimal site occupancies and normalized to 100%. A component is not considered significant unless its value exceeds the uncertainty. [3] B_2O_3 calculated as B = 3.00 *apfu.* [4] The amount of fluorine was determined by F-ion sensitive electrodes on a bulk sample of this crystal. [5] H_2O was determined by U-extraction on a bulk sample of this crystal (average result of two analyses). Mn and Cr were below the detection limit in both samples.

Quadrupole-splitting distributions (*QSD*s) were used to represent the contributions of *Y*-site Fe^{2+} in this spectrum. Following the established conventions for fits using the quadrupole-splitting distribution, γ, which is the Lorentzian full peak-width and half-maximum intensity, was constrained to be 0.20 mm/s, which is roughly the natural linewidth of Fe. The ratio of Lorentzian heights of the two lines in an elemental quadrupole doublet, h_+/h_-, was constrained for all components to be equal to zero. The values for δ_0 (the value of isomer shift, δ, where the distributed hyperfine parameter has a value of zero) and δ_1 (the coupling of δ to the distributed hyperfine parameter) were constrained to be the same (but allowed to vary as a group) for all subcomponents based upon the assumption that these all represent Fe^{2+} atoms at the *Y* site. The remaining parameters, including the center of the Gaussian component of the Δ distribution (Δ_0), the width of the quadrupole-splitting distribution (δ_Δ), and the relative area of the doublets (A), were allowed to vary freely. Isomer shift (δ) is calculated using $\delta = \delta_1 * \Delta_0 + \delta_0$. Details relating to the application of these parameters can be found in Rancourt & Ping (1991).

The parameters of the three modeled Gaussian subcomponents (Table 5) all correspond to Fe^{2+} at the *Y* site, in keeping with the assignments proposed by Pieczka *et al.* (1997) and used by Dyar *et al.* (1998). With varying combinations of constraints for the parameters of each subcomponent, there was no evidence of

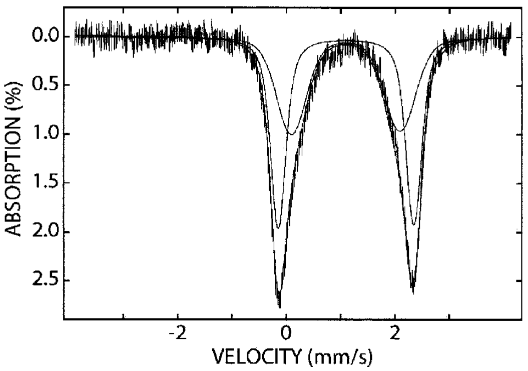

FIG. 1. Room-temperature Mössbauer spectrum of Goslarn olenite, showing two spectral subcomponents arising from a single Gaussian distribution of the quadrupole splitting from Fe^{2+} at the *Y* site.

any contribution from Fe^{3+} in either tetrahedral or octahedral coordination. Similarly, we attempted fits using two *versus* three subcomponents. The total quadrupole-splitting distribution was very similar for both the two-subcomponent fits and the three-subcomponent fits, and it is well defined, independent of the number of Gaussian subcomponents used. This result is typical of the Voigt-based QSD method of fitting used here, which yields results that are quite stable. The chi-squared value for the two-subcomponent fit (0.669) is only slightly different than that of the three-subcomponent fit (0.653), so for the sake of simplicity, we have chosen the two-subcomponent fit for Figure 1 and Table 5.

The parameters of the Fe^{2+} Gaussian subcomponents (Table 5) correspond to Fe^{2+} at the *Y* site, in keeping with the assignments proposed by Pieczka *et al.* (1997) and used by Dyar *et al.* (1998). It must be noted that a different model of fitting (in which a fourth subcomponent for Fe^{3+} was added) was attempted, but it did not yield realistic Mössbauer parameters for $^{[4]}Fe^{3+}$, and the putative Fe^{3+} contribution was very low (roughly 6%). Furthermore, Fe^{3+} was not recognized in the crystal-structure refinement, so the purely $^{Y}Fe^{2+}$ fits were considered to be the most appropriate.

Infrared spectroscopy

The spectrum was collected on Nicolet Nexus FTIR spectrometer (at the National Geophysical Research Institute, Hyderabad) equipped with TEC–DTGS detector and a XT–KBr beam splitter. The spectrometer has a dual source covering a 375 to 11000 wavenumber range. A thin plate (1 mm in size) was broken off the tourmaline crystal described above, and was heated at about 80°C for about 3 h before collecting the IR spectra. A circular aperture (of the same size as the plate) was just covered with the thin plate, and the spectrum was recorded in the range 2000–11000 cm^{-1}. This spectrum was recorded with unpolarized light, covering overtone and combination modes in the range 3000–6000 cm^{-1}.

TABLE 5. MÖSSBAUER PARAMETERS FOR OLENITE FROM GOSLARN, LOWER AUSTRIA

	$^{Y1}Fe^{2+}$	$^{Y2}Fe^{2+}$
γ	0.20	0.20
Δ_0	2.49	2.00
δ_Δ	0.44	1.11
δ_0	1.07	1.07
δ_1	0.01	0.01
δ	1.09	1.09
A	0.53	0.47

Results are given in mm/s relative to the center point of a Fe foil calibration spectrum. γ, which is the Lorentzian full peak-width and half-maximum intensity, was constrained to be 0.20 mm/s, which is the natural linewidth of Fe. Δ_0 is the center of a Gaussian component of the Δ distribution. δ_Δ is the width of the quadrupole splitting distribution. δ_0 is the value of isomer shift, δ, where the distributed hyperfine parameter has a value of zero. δ_1 is the coupling of δ to the distributed hyperfine parameter. $\delta = \delta_1 * \Delta_0 + \delta_0$. A is the relative area of doublet. The ratio of Lorentzian heights of the two lines in an elemental quadrupole doublet, h_+/h_-, was constrained to be equal to zero for all components. Details can be found in Rancourt & Ping (1991). The reduced χ^2 value for this fit was 0.669.

Optimization of site occupancies

Using quadratic programming methods, Wright *et al.* (2000) described a method of optimizing the occupancies of cation sites in minerals having multiply occupied sites. Using that method with the structure refinement and chemical data obtained in this study, the structural formulae of these tourmaline samples are:

GOS1 (rim): $^{X}(Na_{0.71}Ca_{0.10}K_{001}\square_{0.18})$
$^{Y}(Al_{1.42}Mg_{1.10}Fe^{2+}_{0.39}Ti_{0.09})$ $^{Z}(Al_{4.94}Mg_{1.06})$
$^{T}(Si_{5.95}Al_{0.05})$ B_3O_{27} $[(OH)_{3.05}O_{0.92}F_{0.03}]$

GOS2 (core): $^{X}(Na_{0.64}Ca_{0.11}K_{002}\square_{0.23})$
$^{Y}(Al_{1.58}Mg_{0.91}Fe^{2+}_{0.41}Ti_{0.10})$ $^{Z}(Al_{4.90}Mg_{1.10})$
$^{T}(Si_{6.00})$ B_3O_{27} $[(OH)_{3.07}O_{0.90}F_{0.03}]$

The optimized formula essentially minimizes the differences between the formula obtained from the results of the chemical analysis and that obtained by structure refinement. For these optimizations, the bond valences were taken into consideration, but bond lengths were not employed in the refinement.

DISCUSSION OF THE ATOMIC ARRANGEMENT

Hawthorne (1996) noted that the occurrence of Al at the *Y* site and Mg at the *Z* site in tourmaline is due to disorder rather than differences in chemical composition, and that the order–disorder reaction can be expressed in the form $^{Y}Mg + {}^{Z}Al \leftrightarrow {}^{Y}Al + {}^{Z}Mg$ $[^{Y}Mg^{Z}Al(^{Y}Al^{Z}Mg)_{-1}]$. This disorder is driven by the short-range requirements of O^{2-} at the O1 site that is associated with 2Al + Mg configurations at the coordinating *Y* sites so as to satisfy its bond-valence requirements (Hawthorne 1996, 2002). Taylor *et al.* (1995) showed that disorder of Al and Mg over the *Y* and *Z* sites in a calcic tourmaline occurs in tandem with significant O^{2-} at the O1 site. The tourmaline from Goslarn is a good example of a sodic tourmaline wherein the *Y* site is occupied by ~(Al_2Mg), and the *Z* site, by ~(Al_5Mg). The O1 site is occupied by ~$[O_{0.9}(OH)_{0.1}]$, exactly as predicted by Hawthorne (1996) for such a tourmaline. Hawthorne (2002) calculated the bond-valence arrangements for such a tourmaline (his Table 5). Mg-bearing Na-rich tourmaline samples with an Al-dominant *Y* site were previously described by Bloodaxe *et al.* (1999) with $Al_{1.22}$–$Al_{1.28}$ (<*Y*–O> = 2.018–2.025 Å) at the *Y* site and by Ertl *et al.* (2001b) with $Al_{1.36}$ at the *Y* site (<*Y*–O> = 2.012 Å). The tourmaline from Goslarn contains $Al_{1.42}$ at the *Y* site (<*Y*–O> = 2.010 Å) of the rim sample, and $Al_{1.58}$ at the *Y* site (<*Y*–O> = 2.006 Å) of the core sample.

The Mössbauer spectrum (Fig. 1) contains three $^{Y}Fe^{2+}$ doublet components (*Y* sites with different next-nearest neighbors: *Y*1, *Y*2, *Y*3). This interpretation is in agreement with the structural refinement that reveals the absence Fe^{3+} at the *Z* site. The number of electrons (12.94–12.95 e^- by refinement) at the *Z* site is lower than for a complete occupancy by Al (13 e^-). This can only be explained by the occurrence of Mg (12 e^-) at this site. The absence of Fe^{3+} reflects the relatively reducing conditions in a closed magmatic environment (Dyar *et al.* 1998, Fuchs *et al.* 1998, Oliveira *et al.* 2002).

The FTIR spectrum (Fig. 2) of the Goslarn tourmaline shows four bands (~4528, 4457, 4358 and 4241 cm^{-1}) that are combinations due to OH stretch + *M*OH bends. In the fundamental OH-stretching region, only three bands [3737, 3630 (sh) and 3552 cm^{-1}] are clearly observed, and all are comparable with those found in dravite. A broader mode at ~3208 cm^{-1} and a very weak and broad component at ~5177 cm^{-1} could be due to H_2O. It is not clear if the H_2O is present as fluid inclusions or in the structure. Castañeda *et al.* (2000) mentioned that the broad band at ~3170 cm^{-1} (which was observed in samples of the elbaite–schorl series) is probably due to traces of interstitial molecular H_2O (Nakamoto 1970). Similar bands at ~3200 cm^{-1} have been observed by Oliveira *et al.* (2002) for tourmaline samples (elbaite–schorl series) from granitic pegmatites. Tourmaline samples from granitic rocks, from magnesite deposits, and from gold deposits do not show this band at ~3200 cm^{-1} (Oliveira *et al.* 2002). The relatively sharp bands from the Goslarn tourmaline in Figure 2 indicate a higher crystallinity. Strong electronic absorption around 8000–9000 cm^{-1} is indicative of Fe^{2+}. Oliveira *et al.* (2002) observed that a very weak band at 3690 cm^{-1}, observed in tourmaline samples (dravite–schorl series) from gold deposits, might be indicative of O^{2-} at the *W* site, which results in the displacement of Mg to the *Z* site and of Al to the *Y* site. However, our strongly disordered tourmaline sample from Goslarn does not show a band at ~3690 cm^{-1}. We thus disagree that a band at 3690 cm^{-1} indicates O^{2-} at the *W* site. It must thus have another explanation. Castañeda *et al.* (2000) assigned the band at ~3630 cm^{-1} in Fe-rich tourmaline (from granitic pegmatites in Brazil) to the O–H1 stretching with a local environment of $^{Y}Fe^{Y}Fe^{Y}Fe$. The band at ~3630 cm^{-1} (Fig. 2) in the tourmaline sample from Goslarn is relatively small compared to that in the Fe-rich tourmaline samples from Brazil (Castañeda *et al.* 2000). This relatively small band is consistent with the occupancy of ~$[O_{0.9}(OH)_{0.1}]$ at the *W* site (O1 site). Castañeda *et al.* (2000) assigned the band at ~3550 cm^{-1} (samples from the elbaite–schorl series) to the O–H3 stretching with a local environment ^{Y}(Fe,Al) ^{Z}Al ^{Z}Al or ^{Y}R ^{Z}Al ^{Z}Al. In the Goslarn tourmaline, we observed a strong band at ~3552 cm^{-1}, which is in agreement with an occupancy of ~$(OH)_3$ at the *V* site (O3 site).

Using currently valid tourmaline end-member species (Hawthorne & Henry 1999), we can describe the tourmaline samples from Goslarn as a mixture of olenite, dravite and schorl. The core sample (*GOS2*) consists of 53 mol.% olenite, 30% dravite, and 14% schorl. The rim sample (*GOS1*) consists of 47 mol.% olenite, 37% dravite, and 13% schorl. Whereas the olenite component decreases from the core to the rim, the dravite component increases. The schorl component decreases only slightly from the core to the rim. The assumption that all Mg occupies the *Y* site, with none at the *Z* site, would give 67 mol.% dravite for the core sample and 72 mol.% dravite for the rim sample. This choice would result in an incorrect interpretation of these tourmaline samples. The relatively high Al content at the *Y* site in the tourmaline samples from Goslarn is also reflected by the relatively short <*Y*–O> distances (2.006–2.010 Å, Table 3). The shortest <*Y*–O> distances that have been observed in Mg-bearing tourmaline samples so far are 2.021 Å (Grice & Ercit 1993), 2.038 Å (MacDonald & Hawthorne 1995), 2.018 Å (Bloodaxe *et al.* 1999), and 2.012 Å (Ertl *et al.* 2001b).

The Li content of the Goslarn samples is assumed to be very low (< 0.01 wt% Li_2O) because of the absence of any Li-rich minerals (*e.g.,* elbaite, lepidolite) in the pegmatite and because of the very low F content (0.05 wt% F). Lithium and F are usually positively correlated in Li-bearing tourmaline (*e.g.,* data in Dyar *et al.* 1998). In addition, Mg-rich tourmaline with significant Li content is very rare in nature (elbaite–dravite tourmaline from Bližná, Czech Republic; Novák *et al.* 1999). Furthermore, no band at ~3594 cm^{-1} (assigned to O–H3 with a local environment of ^{Y}Li ^{Y}Al ^{Y}*R*; Castañeda *et al.* 2000), and no band at ~3480 cm^{-1} (assigned to O–H3 with a local environment ^{Y}(Al,Mn) ^{Y}Al ^{Y}Li; Grice & Ercit 1993) is visible in the FTIR spectra of the tourmaline from Goslarn (Fig. 2).

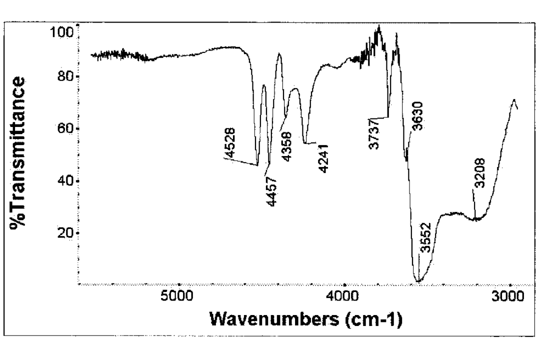

FIG. 2. FTIR spectrum of olenite from Goslarn, Lower Austria (accumulation of 1024 scans, with a resolution of 2 cm^{-1}).

THE ASSIGNMENT OF Mg-RICH TOURMALINE TO DRAVITE OR OLENITE

Determination of the degree of Mg order between the *Y* and *Z* sites without resorting to a crystal-structure refinement and structural-formula optimization would be of interest in tourmaline studies. Hawthorne (2002) showed that a tourmaline with Na at the *X* site and Al_3 or Al_2Mg at the *Y* site requires O^{2-} at the O1 site. Thus, significant F or (OH) content at O1 suggests that the *Y* site is not dominated by Al. If the F content, which can be estimated by EMPA, exceeds 0.5 *apfu*, the Mg-bearing (or Fe^{2+}-bearing) tourmaline will probably not have an Al-dominated *Y* site. Mg-bearing tourmaline with a total (OH) content [or (OH) + F] of ~4 *apfu* will probably not have an Al-dominant *Y* site. Determination of H_2O content in a tourmaline sample is not possible by EMPA, but it is generally worthwhile to undertake such an analysis by SIMS or other techniques.

Hawthorne *et al.* (1993), Grice & Ercit (1993), and MacDonald & Hawthorne (1995) have shown that Mg can occur at the *Z* site in tourmaline and that the variation in <Z–O> distance is a function of constituent-cation radius. Methods to approximate the Mg content at the *Z* site without requiring crystal-structure refinement were given by Grice & Ercit (1993) and Bloodaxe *et al.* (1999). Grice & Ercit (1993) noted a good correlation between the partitioning behavior of Mg and total Fe/(Fe + Mg), but the *Y*-site Mg content can only be reliably calculated for compositions with FeO (total) greater than 7 wt%. Bloodaxe *et al.* (1999) showed that in their samples (dravite–schorl series), the amount of Mg at the *Z* site increases, whereas Fe^{2+} at the *Y* site decreases. Bloodaxe *et al.* (1999) proposed that the occurrence of an Fe^{2+} atom at a *Y* site may be locally associated with the absence of Mg at both of the neighboring *Z* sites, as substitution of Fe^{2+} at *Y* and Mg at *Z* requires antithetic shifts of the O6 anion. Using Figure 3 (Mg at *Z versus* Fe^{2+} at *Y*) in Bloodaxe *et al.* (1999), we can assign ~0.9 *apfu* Mg at the *Z* site for ~0.4 *apfu* Fe^{2+} at the *Y* site of the Goslarn tourmaline samples, which is in good agreement with the optimized formulae for *GOS1* and *GOS 2*.

Another possible method to approximate the Mg content at the *Y* site is to determine the unit-cell parameters. Using our data and those of Bloodaxe *et al.* (1999), the parameter *c* of Mg- (and Fe-) bearing tourmaline samples that contain ~0.9–1.1 *apfu* Mg at the *Z* site is in the range 7.176–7.199 Å. These tourmaline samples do not contain Fe^{3+} at the *Z* site [tourmaline samples that contain significant Fe^{3+} at the *Z* site have high Fe contents (FeO_{tot} >14 wt%; Cámara *et al.* 2002) and are not common]. Using the data of Bloodaxe *et al.* (1999), the *c* parameter of Mg- (and Fe-) bearing tourmaline that contains ~0.6–0.7 *apfu* Mg at the *Z* site is in the range 7.157–7.169 Å, and for samples with ~0.4–0.5 *apfu* Mg at the *Z* site, it is the range 7.146–7.154 Å. After subtracting the amount of Mg at the *Z* site from the total Mg (*apfu*), the rest will occupy the *Y* site. For the most common tourmaline samples, this procedure will approximate the degree of Al–Mg order where there is no possibility for a single-crystal structure refinement.

SUMMARY

We have described an example of disordered Mg-bearing olenite with up to $\sim Al_{1.6}$ at the *Y* site (<*Y*–O> = 2.006 Å) and $\sim Mg_{1.1}$ at the *Z* site (<*Z*–O> = 1.926 Å). The O1 site is occupied by $\sim[O_{0.9}(OH)_{0.1}]$, and the O3 site is occupied by $(OH)_3$. No Fe^{3+} was found by Mössbauer spectroscopy or by refinement (at the *Z* site). The disorder in the distribution of Mg in the Goslarn tourmaline is further supported by the relatively small band at ~3630 cm^{-1}, which can be assigned to the O–H1 stretching. This tourmaline from a granitic pegmatite near Goslarn, Lower Austria, is a good example of disorder driven by the short-range requirements of O^{2-} at the O1 site associated with 2Al + Mg configurations at the coordinating *Y* sites.

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