American Mineralogist, Volume 95, pages 1467–1472, 2010

On the crystal chemistry of londonite [(Cs,K,Rb)$Al_4Be_5B_{11}O_{28}$]: A single-crystal neutron diffraction study at 300 and 20 K

G. Diego Gatta,[1,2,*] Pietro Vignola,[1,2] Garry J. McIntyre,[3] and Valeria Diella[1,2]

[1]Dipartimento di Scienze della Terra, Università degli Studi di Milano, Via Botticelli 23, I-20133 Milano, Italy
[2]CNR-Istituto per la Dinamica dei Processi Ambientali, Via Mario Bianco 9, I-20131 Milano, Italy
[3]Institut Laue-Langevin, BP 156, 38042 Grenoble Cedex 9, France

Abstract

The crystal chemistry of londonite, a rare Cs-bearing mineral [ideal chemical formula: (Cs,K) $Al_4Be_4(B,Be)_{12}O_{28}$; a = 7.3098(2) Å at 300 K, space group $P\bar{4}3m$] from the granitic pegmatites of the Antsongombato Gem Mine, Betafo district, Madagascar, has been reinvestigated by means of wavelength dispersive X-ray spectroscopy, laser ablation-inductively coupled plasma-mass spectroscopy, inductively coupled plasma-atomic emission spectroscopy, X-ray powder diffraction, and single-crystal neutron diffraction at 300 and 20 K. Single-crystal anisotropic structural refinement at 300 K gave a final agreement index R_1 = 0.0479 for 32 refined parameters and 416 unique reflections with $F_o > 4\sigma(F_o)$. The analysis of the difference-Fourier maps of the nuclear density discounts the presence of hydroxyl groups, as wrongly reported in some of the previous studies. The structural refinements and the chemical analyses suggested that: the tetrahedral 4*e* site (at $x \sim 0.258$) is mainly occupied by Be, but a low amount of B (~3%) likely occurs; the tetrahedral 12*h* site (at $x \sim 0.248$) is mainly occupied by B, but a significant fraction of Be (~12%) is present; the octahedral 4*e* site (at $x \sim 0.361$) is fully occupied by Al; and the 1*a* site (at $x = 0$, with CN = 12) is mainly occupied by Cs, with Rb and K. The significantly high amount of B_2O_3 (~50 wt%) and Cs+Rb($CsO_2+RbO_2 \geq 8$ wt%) makes the synthetic counterpart of londonite of interest as a potential neutron absorber or a potential host for nuclear waste.

Keywords: Londonite, crystal chemistry, crystal structure, single-crystal neutron diffraction, low temperature

Introduction

Londonite is a rare Cs-bearing mineral with ideal chemical formula (Cs,K)$Al_4Be_4(B,Be)_{12}O_{28}$ (with Cs > K, Simmons et al. 2001). The K-dominant analog is rhodizite. Londonite and rhodizite have been found in lithium-cesium-tantalum (LCT) granitic pegmatites in a few localities worldwide (Simmons et al. 2001). Whereas rhodizite was described for the first time by Rose in 1834, londonite has only been recently approved by the Committee on New Minerals and Mineral Names of the International Mineralogical Association (IMA number 1999-014) (Simmons et al. 2001). This mineral is extremely rare. It has been found only at three pegmatite mines in Madagascar. Laurs et al. (2002) reported that gem-quality rhodizite-londonite crystals are known only from the Antsongombato pegmatite in the Betafo region, Madagascar.

The crystal chemistry and crystal structure of rhodizite have been the subjects of several investigations. However, the real chemical composition of rhodizite has been a matter of debate for about a century. Duparc et al. (1911) reported the formula of rhodizite as $(Li,K,Cs,Rb,Na,H)_4Al_6Be_7B_{14}O_{39}$. Later, Lacroix (1922) suggested a different formula: $(Cs,Rb,K,Na,H)_8Al_6Be_4B_{12}O_{35}$. Strunz (1938) described rhodizite as an anhydrous mineral, with chemical formula: $NaKLi_4Al_4Be_3B_{10}O_{27}$. More recently, Frondel and Ito (1965) provided the chemical analysis of a Cs-rich rhodizite from Manjaka, Madagascar, and reported the formula: (Cs,K)$Al_4Be_4B_{11}O_{25}(OH)_4$. New insight into the crystal chemistry of rhodizite came from the experiment of Taxer and Buerger (1967), who finally solved and refined the crystal structure of the rhodizite from Manjaka by single-crystal X-ray diffraction and provided the anhydrous chemical formula: $CsAl_4Be_4B_{12}O_{28}$. However, such a formula appeared to be unbalanced, requiring a neutral Cs atom. Further experiments by Donnay et al. (1966, 1967) based on electron-spin-resonance spectroscopy showed the cationic nature of Cs, and the authors suggested the hydrous formula $CsAl_4Be_4B_{11}O_{26}(OH)_2$. Only more recently, Pring et al. (1986) reinvestigated the crystal chemistry and the crystal structure of a K-dominant rhodizite from Ambatofinandrahana, Madagascar, by high-resolution electron microscopy (HREM), magic-angle-spinning nuclear magnetic resonance (MAS-NMR), atomic absorption spectrophotometry, inductively coupled plasma emission spectrometry, CHN-elemental analysis, and a structure refinement by single-crystal X-ray diffraction. The formula reported by Pring et al. (1986) was: $(K_{0.46}Cs_{0.36}Rb_{0.06}Na_{0.02})_{\Sigma0.90}Al_{3.99}Be_4(B_{11.35}Be_{0.55}Li_{0.02})_{\Sigma11.92}O_{28}$. No evidence of molecular water or hydroxyl groups have been found. The crystal structure of rhodinzite was refined on the basis of the structure model previously reported by Taxer and Buerger (1967), with a = 7.318(1) Å and space group $P\bar{4}3m$. The building block units of the structure of rhodizite are represented by

---

* E-mail: diego.gatta@unimi.it

0003-004X/10/0010–1467$05.00/DOI: 10.2138/am.2010.3554

clusters of four edge-sharing Al-octahedra (with Al at a 4*e* site, $x \sim 0.361$), linked to B- and Be-tetrahedra (12*h* site at $x \sim 0.248$ and 4*e* site at $x \sim 0.258$, respectively) with a configuration like that shown in Figure 1. Be- and B-tetrahedra form rows parallel to <110>. The alkali cations lie at the unit-cell origin and occupy cavities of approximately tetrahedral geometry with coordination number CN = 12 (1*a* site, $x = 0$). The X-ray structure refinement of Pring et al. (1986) was conducted assuming (and not refining) the distribution of the boron and beryllium between the 12*h* and the 4*e* sites. Several distribution models with fixed occupancies were considered. The best fit was obtained with the Taxer and Buerger (1967) model, with the B atoms assigned to the 12*h* sites, full Be occupancy of the 4*e* sites, and the remainder of the Be in the 12*h* sites. This model agrees with the distribution of boron and beryllium deduced by MAS-NMR, as the spectra for both elements gave only single resonances indicating that all beryllium and boron atoms are located in chemically equivalent sites.

A structural refinement of londonite has not been reported so far, although the crystal chemistry of the "rhodizite" sample used by Taxer and Buerger (1967) appears to be similar to that expected for londonite, rather than for rhodizite. Despite the structural model of Taxer and Buerger (1967) and Pring et al. (1986) for rhodizite being quite plausible, the authors were not able to refine the anisotropic displacement factors of the atomic sites (allowed by symmetry) and the B/Be-distribution in the tetrahedral sites. In this light, the aim of the present study is an investigation of the crystal chemistry and crystal structures of londonite from the granitic pegmatites of the Antsongombato Gem Mine, Betafo district, Madagascar, by means of wavelength dispersive X-ray spectroscopy, laser ablation-inductively coupled plasma-mass spectroscopy, inductively coupled plasma-atomic emission spectroscopy, X-ray powder diffraction, and single-crystal neutron diffraction at 300 and 20 K. Previous X-ray single-crystal diffraction studies of rhodizite have proved to be insufficient to provide a unique picture of the B/Be-distribution in the tetrahedral sites or to exclude the presence of possibly disordered H atoms. On this basis, single-crystal neutron diffraction represents the best experimental technique that allows one to answer the open questions about the crystal structure and crystal chemistry of londonite.

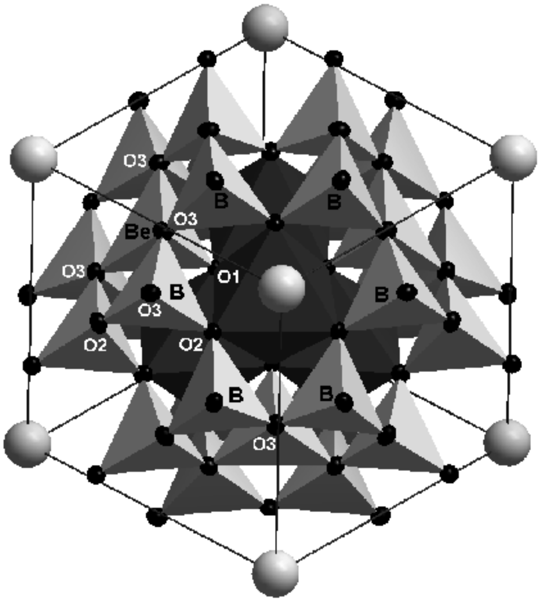

FIGURE 1. Clinographic view of the crystal structure of londonite. B-rich (12*h*) and Be-rich (4*e*) tetrahedra are shown in light gray, and Al (4*e*) octahedra in dark gray. The large spheres represent the alkali (1*a*) site.

Samples description and mineralogy

Natural samples of londonite coming from the LCT granitic pegmatites of the Antsongombato Gem Mine, Betafo district, Madagascar, were used for the experiments of the present study. The granitic pegmatites of the Antsongombato Gem Mine, that form dikes from a few centimeters to over 2 m wide and up to 300 m long, are hosted along the metamorphic foliation of dolomitic marbles belonging to the metasedimentary rocks of the Itremo Group (Pezzotta 2001, 2005). These pegmatites are characterized by high boron enrichment, as confirmed by the significant presence of danburite, tourmaline-group minerals, rhodizite-londonite, behierite-schiavinatoite, dumortierite, and ambergite, and belong to the "Danburite Subtype of the Rare Element Class granitic pegmatites" with LCT geochemical signature (e.g., Pezzotta 2001, 2005). Londonite occurs in the central and highly evolved portions of the dikes, rich in red tourmalines and in close association with behierite-schiavinatoite and Cs-bearing minerals like pollucite (Pezzotta 2001; Simmons et al. 2001; Demartin et al. 2001).

The samples used for the chemical analyses and the neutron diffraction experiment were cut from a deep-yellow, gem-quality londonite dodecahedron of 16 mm in diameter. The londonite crystal was hosted into the central part of a 3.5 cm wide pegmatitic dike and associated with deep-red tourmaline, danburite, and pollucite.

EXPERIMENTAL METHODS

Quantitative electron microprobe analyses were performed on polished samples of londonite using a JEOL JXA-8200 microprobe in wavelength dispersive mode at the Earth Sciences Department, University of Milano (ESD-MI). The system was operated using an accelerating voltage of 15 kV, a beam current of 15 nA and beam diameter of 5 μm, and a counting time of 30 s on the peaks and 10 s on the background. Natural minerals (anorthite for Al, K-feldspar for K, pollucite for Cs and Rb, fayalite for Fe, and forsterite for Mg) were used as standards. The raw data were corrected for matrix effects using the ΦρZ method as implemented in the JEOL suite of programs.

A further series of chemical analyses by laser ablation-inductively coupled plasma-mass spectroscopy (LA-ICP-MS) were performed at the CNR-IGG laboratories in Pavia, on the same crystal fragments previously analyzed by EMPA-WDS, using an Elan DRC-e mass spectrometer coupled with a Q-switched Nd:YAG laser source (fundamental emission 1064 nm, converted to 266 nm by two harmonic generators). Helium was used as a carrier gas, mixed with an Ar stream in the ablation cell. The following elements were analyzed: Si, Li, Be, Ca, Na, Ti, Mn, Pb, and Ba. The concentration of Li was also measured using a Perkin Elmer 2380 atomic absorption spectrometer (AAS) at the ESD-MI, giving the same result obtained by LA-ICP-MS.

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) was used to analyze B at the ESD-MI. The 100 mg of finely ground londonite was fused with 400 mg of sodium carbonate + sodium hydroxide (1:1) at near 900 °C for 30 min. The resultant glass was dissolved in nitric acid (1 *N*), filtered and then the amount of B was measured by ICP-AES. The precipitate was made only by BeO, as checked by X-ray powder diffraction. The final chemical formula of londonite based on EMPA-WDS, LA-ICP-MS, and ICP-AES is given in Table 1.

Four single crystals of londonite were first inspected on the neutron Laue diffractometer OrientExpress at the Institut Laue-Langevin (ILL), Grenoble (Ouladdiaf et al. 2006). The Laue patterns indicated that all crystals were of very good quality, but the individual Laue spots, which are effectively projected topographs, showed strong absorption in the bulk of each crystal. Crushing one of these crystals yielded a roughly half-cylindrical oblong crystal of maximum dimensions $2.5 \times 2 \times 1.5$ mm^3 that gave a good Laue pattern with single spots of reasonably uniform intensity. Neutron diffraction data for this samples were measured at 300 and 20 K on the four-circle diffractometer D9 at ILL, in a beam of wavelength 0.7058(1) Å obtained by reflection from a Cu (220) monochromator. D9 is equipped with a small two-dimensional area detector (Lehmann et al. 1989), which for this measurement allowed observation of the centroids of all scanned reflections and optimal delineation of the peak from the background. Most reflections of the type $+h$ $+k$ $+l$ to 1.09 Å^{-1} in $\sin\theta/\lambda$ were scanned at both temperatures to give two to three equivalents for most unique reflections. For all data, background corrections following Wilkinson et al. (1988) and Lorentz corrections were applied. Absorption corrections were made by Gaussian integration (Coppens et al. 1965) using the calculated attenuation coefficient $\mu = 0.8557$ mm^{-1}, to give transmission ranges of 0.202–0.308 and 0.207–0.304 at 300 and 20 K, respectively. Initial structural refinements with SHELX-97 (Sheldrick 1997) showed that extinction was quite severe, but could be reasonably well accounted for by the Larson-like correction (Larson 1967) implemented in SHELX-97. Even though both absorption and extinction were quite severe, the roughly isotropic crystal form and the limiting of the data collections to one quadrant meant that the data for both samples could be averaged over symmetry-equivalent reflections; averaging of the 1555/653 reflections scanned at 300/20 K in the Laue group $m3m$ gave 480/377 unique reflections with internal agreement indices of 7.9/5.9%. Least-squares matching of the observed and calculated centroids of the 450 strongest reflections at 300 K gave the lattice constant $a = 7.3098(2)$ Å, and the 221 strongest reflections at 20 K gave $a = 7.3094(4)$ Å excluding the uncertainty in the wavelength. The reflection conditions agreed with the space group $P\bar{4}3m$. Other details pertaining to the data collections are listed in Table 2.

A further X-ray powder diffraction pattern of londonite was collected using a high-resolution Panalytical X'pert Pro X-ray powder diffractometer equipped with a Ni-filtered Cu*K*α-radiation and a X'Celerator-type detector. Operating conditions were: filtered Cu*K*α radiation, 40 kV, 40 mA, 2θ range from 5 to 120°, step size of $2\theta = 0.017°$, counting time of 80 s per step. The unit-cell parameter was refined by Le Bail full-profile fit (Le Bail et al. 1988) using the package GSAS (Larson and Von Dreele 1994), giving: $a = 7.3161(6)$ Å. Silicon NIST 640c was used as internal standard. Observed and calculated *d*-spacings are listed in Table 3.

Structure refinement

The neutron diffraction data of londonite collected at 300 K were first processed with the program E-STATISTICS and ASSIGN-SPACEGROUP, implemented in the WinGX suite of programs (Farrugia 1999), aimed to calculate the normalized structure factors (E's) and their statistics of distributions and providing the highly likely space group. The structure of londonite was found to be centrosymmetric at 26.7% likelihood. Sheldrick's $|E^2 - 1|$ criterion (Sheldrick 1997) provides a further indication of the lack of an inversion center ($|E^2 - 1| = 0.640$, cf. ideal values of 0.968 and 0.736 for centrosymmetric and non-centrosymmetric structures, respectively). Two possible space groups (both belonging to the $m3m$ Laue class) were selected by the program: $Pm\bar{3}m$ and $P\bar{4}3m$. The combined figure of merit suggested the space group $P\bar{4}3m$ as highly likely. The anisotropic crystal structure refinement was then performed in the acentric space group $P\bar{4}3m$ using the SHELX-97 software (Sheldrick 1997), starting from the structure model of Pring et al. (1986). The following bound coherent scattering lengths (b_c in fm) have been used: $b_c(\mathrm{Cs}) = 5.42$, $b_c(\mathrm{Rb}) = 7.08$, $b_c(\mathrm{K}) = 3.67$, $b_c(\mathrm{Li}) = -1.90$, $b_c(\mathrm{Al}) = 3.449$, $b_c(\mathrm{Be}) = 7.79$, $b_c(\mathrm{B}) = 5.30$, and $b_c(\mathrm{O}) = 5.805$ (Sears 1986). The secondary isotropic extinction effect was corrected according to Larson's protocol (Larson 1967), as implemented in the SHELXL-97 package (Sheldrick 1997).

The first cycles of the structure refinement were conducted assigning: (1) Al to the octahedral 4*e* site (at $x \sim 0.361$); (2) Be to the tetrahedral 4*e* site (at $x \sim 0.258$); (3) B to the tetrahedral 12*h* site (at $x \sim 0.248$), and a mixed scattering length Cs (40%) + Rb(20%) + K(40%) to the 1*a* site (at $x = 0$), according to the chemical analysis. However, the refinement did not achieve convergence as the observed nuclear density at the tetrahedral 12*h* site suggested the presence of Be with B, as previously suggested (Pring et al. 1986). In addition, the occupancy factor of the 4*e* site (at $x \sim 0.258$), modeled as fully occupied only by Be, tended to be slightly, but significantly, lower than 100%. The octahedral site was found to be fully occupied by Al and the residuals in the difference-Fourier map of the nuclear density function showed a site occupancy of ~86% of the alkali 1*a* site, assuming the mixed scattering length aforementioned. On this basis, further refinement cycles were conducted using a different scheme of the cation distribution on the tetrahedral sites: the tetrahedral 4*e* and 12*h* sites were modeled as occupied by Be+B. With such a configuration, convergence was rapidly achieved. The principal mean square atomic displacement parameters were positively defined and the variance-covariance matrix showed no significant correlation among the refined parameters. At the end of the last cycle of refinement, no peak larger than +1.8/–1.6 fm/Å^3 was present in the final difference-Fourier map of the nuclear density (Table 2). The final agreement index was $R_1 = 0.0479$ for 32 refined parameters and 416 unique reflections with $F_o > 4\sigma(F_o)$ (Table 2). Atomic coordinates, site occupancy factors, and thermal displacement parameters are reported in Table 4a. Bond lengths and angles are listed in Table 5.

The neutron diffraction data of londonite collected at 20 K were processed following the same strategy already adopted for those at 300 K. The structure refinement at 20 K was performed starting from the refined structure model at 300 K. The lower number of reflections scanned and the drastic reduction of the magnitude of the thermal displacement parameters, toward a quasi-isotropic displacement regime, led us to use isotropic displacement factors for the tetrahedral 12*h* and 4*e*, octahedral

TABLE 1. Representative composition of londonite based on LA-ICP-MS, ICP-AES, and EMPA-WDS

	wt%	e.s.d.	Cations (apfu) on the basis of 28 O	
SiO_2*	0.10	(0.11)	Si	0.014
B_2O_3†	48.91	(0.87)	B	11.15
Al_2O_3‡	24.40	(0.53)	Be	4.82
Fe_2O_3‡	0.23	(0.15)	Al	3.82
BeO*	15.11	(0.48)	Fe^{3+}	0.02
MgO‡	0.01	(0.12)	Li	0.05
CaO*	0.26	(0.16)	Ca	0.04
Na_2O*	0.06	(0.18)	Na	0.02
K_2O‡	2.03	(0.37)	K	0.34
Rb_2O‡	1.80	(0.92)	Rb	0.15
Cs_2O‡	6.32	(0.85)	Cs	0.36
Li_2O*	0.19	(0.09)		
Total	99.42			

* By LA-ICP-MS (av. 6 analyses).

† By ICP-AES (av. 3 analyses).

‡ By EMPA-WDS (av. 10 analyses); the following trace elements were also measured: Ti 41 wt. ppm, Pb 46 wt. ppm, Mn 4 wt. ppm, and Ba 2 wt. ppm.

TABLE 2. Details of neutron data collection and refinement of londonite at 300 and 20 K

T (K)	300	20
Crystal shape	Irregular half cylinder	Irregular half cylinder
Crystal size (mm^3)	~7.5	~7.5
Crystal color	Translucent yellow	Translucent yellow
Unit-cell parameters	$a = 7.3098$ (2) Å $V = 390.59$ Å^3	$a = 7.3094(4)$ Å $V = 390.52$ Å^3
No. of reflections for cell parameters	450	221
Representative chemical formula	$(Cs,K,Rb)Al_4Be_5B_{12}O_{28}$	$(Cs,K,Rb)Al_4Be_5B_{12}O_{28}$
Space group	$P\bar{4}3m$	$P\bar{4}3m$
Z	1	1
Radiation (Å)	0.7058(1)	0.7058(1)
Diffractometer	D9 four circle	D9 four circle
Data collection method	ω-θ scans	ω-θ scans
Max. θ (°)	50	50
	$0 \le h \le 15$	$-2 \le h \le 13$
	$0 \le k \le 15$	$-2 \le k \le 15$
	$-9 \le l \le 11$	$-2 \le l \le 8$
No. of standard reflections	1	1
Frequency of standard reflections	Every 50 reflections	Every 50 reflections
No. measured reflections	1427	578
No. unique reflections	455	347
No. unique refl. with $F_o > 4\sigma(F_o)$	416	317
No. refined parameters	32	20
R_{int}	0.0793	0.0589
Refinement on	F^2	F^2
$R_1(F)$ with $F_o > 4\sigma(F_o)$	0.0479	0.0510
$R_1(F)$ for all the unique reflections	0.0534	0.0578
$wR_2(F^2)$	0.0936	0.0881
GooF	1.570	1.311
Weighting scheme: a, *b*	0.01,0	0.01,0
Residuals (fm/Å^3)	+1.8/–1.6	+1.2/–1.2

Note: $R_{int} = \Sigma|F_o^2 - F_o^2(\mathrm{mean})|/\Sigma[F_o^2]$; $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$, $w = 1/[\sigma^2(F_o^2) + (a*P)^2 + b*P]$, $P = [\mathrm{Max}(F_o^2,0) + 2*F_c^2]/3$.

TABLE 3. X-ray powder diffraction data of londonite investigated in this study

I/I_0	d_{obs} (Å)	d_{calc} (Å)	*hkl*
56.4	7.3152(10)	7.3138	100
8.34	5.1740(16)	5.1717	110
1.34	4.2218(6)	4.2227	111
9.55	3.6611(29)	3.6569	200
35.92	3.2719(7)	3.2709	210
100	2.9867(6)	2.9859	211
4.33	2.5864(4)	2.5858	202
32.81	2.4385(4)	2.4379	300, 221
0.29	2.3123(4)	2.3128	301
22.89	2.2057(3)	2.2052	311
40.4	2.1117(3)	2.1113	222
1.9	2.0288(2)	2.0285	320
20.84	1.9550(2)	1.9547	321
18.5	1.8288(2)	1.8285	400
16.28	1.7742(3)	1.7739	401, 223
11.77	1.7242(2)	1.7239	303, 411
0.35	1.6788(6)	1.6779	331
0.69	1.6374(14)	1.6354	424
2.35	1.5963(2)	1.5960	421
4.87	1.5596(2)	1.5593	323
1.68	1.4932(2)	1.4929	422
1.85	1.4630(1)	1.4628	500, 403
5.09	1.4347(2)	1.4344	510, 431
3.91	1.4078(2)	1.4075	511, 333
0.45	1.3598(12)	1.3581	423
1.98	1.3583(1)	1.3581	520
1.78	1.3357(3)	1.3353	512
15.29	1.2932(2)	1.2929	440
1.05	1.2735(2)	1.2732	414, 225
1	1.2546(2)	1.2543	530, 433
0.35	1.2374(8)	1.2363	315
0.34	1.2173(12)	1.2190	600, 424
2.64	1.1868(2)	1.1865	611, 325
2.21	1.1425(2)	1.1422	405, 434
0.76	1.1289(2)	1.1286	415
0.45	1.1157(3)	1.1154	335
1.59	1.1029(2)	1.1026	622
0.76	1.0906(2)	1.0903	630, 425
1.71	1.0786(2)	1.0784	613
0.35	1.0562(4)	1.0557	444
0.31	1.0451(2)	1.0448	700, 623
0.11	1.0349(4)	1.0343	710, 505, 543
0.37	1.0243(1)	1.0241	711, 551
0.22	1.0090(31)	1.0046	416
0.64	1.0049(2)	1.0046	702
0.98	0.9956(2)	0.9953	217, 633, 552
0.39	0.9751(16)	0.9774	642
0.54	0.9690(2)	0.9687	227, 544
0.78	0.9606(1)	0.9604	730
0.2	0.9525(2)	0.9522	731, 535
0.16	0.9366(1)	0.9364	506, 436
0.99	0.9291(2)	0.9289	651, 732
0.4	0.9147(3)	0.9142	800
0.86	0.9075(2)	0.9072	810, 740, 652
0.7	0.9005(1)	0.9003	811, 714, 545
0.02	0.8927(6)	0.8935	337

Note: The refined unit-cell constant is $a = 7.3161(6)$ Å.

4*e*, and O1 sites (Table 4b). As the refined site occupancy factors were found to be similar to those at 300 K (within 1σ), they were fixed to the values refined at 300 K. When convergence was achieved, the variance-covariance matrix showed no significant correlation among the refined parameters, and no peak larger than +1.2/–1.3 fm/Å^3 was present in the difference-Fourier map of the nuclear density (Table 2). The final agreement index was $R_1 = 0.0510$ for 20 refined parameter and 317 unique reflections with $F_o > 4\sigma(F_o)$ (Table 2). Site coordinates and displacement parameters are listed in Table 4b. Bond lengths and angles are given in Table 5.

DISCUSSION AND CONCLUSIONS

This multi-methodological study allowed us to report the first full structure refinement of londonite, and to reinvestigate the chemical formula of this rare mineral.

The structure refinements provided a picture of the distribution of B and Be between the tetrahedral 12*h* and 4*e* sites: (1) the tetrahedral 4*e* site (at $x \sim 0.258$) is mainly occupied by Be, but a low amount of B (~3%) likely occurs, and (2) the tetrahedral 12*h* site (at $x \sim 0.248$) is mainly occupied by B, but a significant fraction of Be (~12%) is present. The octahedral 4*e* site (at $x \sim 0.361$) is fully occupied by Al, whereas the 1*a* site (at $x = 0$) is mainly occupied by Cs, Rb, and K.

The refined site positions in this study are in good agreement with those previously reported for rhodizite by Taxer and Buerger (1967) and Pring et al. (1986), giving an almost undistorted B-rich tetrahedra ($\Delta_{max} \sim 0.011$ Å), a significantly distorted Be-rich tetrahedra ($\Delta_{max} \sim 0.084$ Å), and a regular Al-octahedra ($\Delta_{max} < 0.01$ Å). The shortest Be-O bond distances is observed for the bridging oxygen between the Be-tetrahedron and the Al-octahedron (i.e., O1; Fig. 1; Table 4a). The bonding topology found for londonite in this study is identical to that described for rhodizite by Taxer and Buerger (1967) and Pring et al. (1986).

The magnitude of the thermal displacement parameters of the bridging oxygen O1 is lower than those of the other oxygen sites (i.e., U_{ij} of O2 and O3; Table 4a). As reported in the previous investigations of the rhodizite structure, also in londonite we observe a partial site occupancy at the alkali 1*a* site (~86%; Table 4a). In addition, the thermal displacement parameter (isotropic by symmetry, U_{iso}) is one order of magnitude higher than those of the other sites (Table 4a). Such a result would be explained by the large cavity in which the alkali site lies and also by the presence of a significantly high number of elements that share the site (i.e., Cs, Rb, K, Na, and Ca), each with a slightly different preferred bonding configuration. On the whole, the refined 1*a* site thermal displacement parameter reflects disorder around the 0,0,0 position, probably both static and dynamic, and likely due to the multi-element site distribution. Evidence of ordering at the 1*a* site was not observed, as also reported by Pring et al. (1986) in rhodizite.

The low-*T* structure refinement shows that at 20 K the symmetry and the structure model of londonite described at 300 K is preserved (Tables 4a, 4b, and 5). A significant decrease of the thermal displacement parameters is observed. However, the alkali 1*a* site maintains a U_{iso} value of about one order of magnitude higher than those of the other atomic sites (Table 4b).

The chemical analyses (Table 1) show a low presence of Si (~0.014 apfu), which likely replaces B at the 12*h* site. Lithium (~0.05 apfu) likely replaces B at the 12*h* site or Al at the octahedral 4*e* site (Pring et al. 1986; Simmons et al. 2001). Iron (~0.05 apfu) would share with Al the octahedral 4*e* site. Calcium (~0.04 apfu) and Na (~0.02 apfu) likely lie at the 1*a* site with Cs, K, and Rb. On the basis of the cation partitioning derived by the neutron structure refinement (in particular the refined occupancy factor of beryllium at the B-rich 12*h* site, Table 4a), the empirical chemical formula of londonite (on the basis of 28 oxygen apfu) may be written as: ${}^{1a}(Cs_{0.36}K_{0.34}Rb_{0.15}Ca_{0.04}Na_{0.02})_{\Sigma 0.91}{}^{4e}(Al_{3.82}Li_{0.05}Fe_{0.02})_{\Sigma 3.89}{}^{4e}(Be_{3.82}B_{0.18})_{\Sigma 4}{}^{12h}(B_{10.97}Be_1Si_{0.01})_{\Sigma 11.98}O_{28}$. Therefore, we suggest the following ideal chemical formula of londonite: $(Cs,K,Rb)Al_4(Be,B)_4(B,Be)_{12}O_{28}$. It is interesting to point out that the partial occupancy of the alkali 1*a* site is observed by both chemical analyses (Σ0.91) and neutron structure refinement (s.o.f. ~ 0.86; Table 4a).

TABLE 4a. Refined positional and thermal displacement parameters (Å^2) of londonite at 300 K

Site	Site occupancy factor	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{iso}/U_{eq}
(1*a*) Alkali	$(Cs_{0.4}Rb_{0.2}K_{0.4})$ 86(5)%	0	0	0							0.023(2)
(4*e*) Al	Al 100%	0.3608(2)	0.3608(2)	0.3608(2)	0.0020(3)	0.0020(3)	0.0020(3)	–0.0001(3)	–0.0001(3)	–0.0001(3)	0.0020(3)
(12*h*) B	B 88(2)%, Be 12(2)%	0.24835(15)	1/2	0	0.0031(3)	0.0030(3)	0.0022(3)	0	0	–0.0002(2)	0.0028(2)
(4*e*) Be	Be 97(2)%, B 3(2)%	0.25833(11)	0.74167(11)	0.25833(11)	0.0036(3)	0.0036(3)	0.0036(3)	0.0001(2)	–0.0001(2)	0.0001(2)	0.0036(3)
(4*e*) O1	O 100%	0.38103(14)	0.61897(14)	0.38103(14)	0.0023(2)	0.0023(2)	0.0023(2)	0.0003(2)	–0.0003(2)	0.0003(2)	0.0023(2)
(12*i*) O2	O 100%	0.36350(12)	0.36350(12)	0.09976(14)	0.0045(2)	0.0045(2)	0.0027(3)	0.0007(3)	0.0003(2)	0.0003(2)	0.0039(2)
(12*i*) O3	O 100%	0.39923(14)	0.86485(11)	0.13515(11)	0.0046(2)	0.0037(3)	0.0037(2)	–0.0004(2)	0.0004(3)	0.0001(2)	0.0040(1)

Notes: A mixed scattering length [Cs(40%)+Rb(20%)+K(40%)] was used at the 1*a* site (at $x = 0$), according to the chemical analysis. The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2U_{11} + \ldots + 2hka^*b^*U_{12}]$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 4b. Refined positional and thermal displacement parameters (Å^2) of londonite at 20 K

Site	Site occupancy factor	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{iso}/U_{eq}
(1*a*) Alkali	$(Cs_{0.4}Rb_{0.2}K_{0.4})$ 86%	0	0	0							0.010(1)
(4*e*) Al	Al 100%	0.3603(3)	0.3603(3)	0.3603(3)							0.0012(1)
(12*h*) B	B 88%, Be 12%	0.24846(16)	1/2	0							0.0012(1)
(4*e*) Be	Be 97%, B 3%	0.74190(11)	0.25810(11)	0.25810(11)							0.0012(1)
(4*e*) O1	O 100%	0.38070(16)	0.61930(16)	0.38070(16)							0.0012(1)
(12*i*) O2	O 100%	0.36390(12)	0.36390(12)	0.10010(16)	0.0021(2)	0.0021(2)	0.0014(3)	0.0009(3)	0.0004(2)	0.0004(2)	0.0019(2)
(12*i*) O3	O 100%	0.39899(17)	0.86510(12)	0.13490(12)	0.0023(2)	0.0025(3)	0.0025(2)	–0.0001(2)	0.0001(3)	0.0002(2)	0.0024(2)

Notes: The site occupancy factors were fixed to the values refined at 300 K (see text for further details). The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2U_{11} + \ldots + 2hka^*b^*U_{12}]$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. One isotropic displacement parameter was used for the Al, B, Be, and O1 sites.

TABLE 5. Relevant bond distances (Å) and angles (°) in the londonite structure at 300 and 20 K

T = 300 K				T = 20 K			
Be-O1	1.553(1)	O3-Be-O3	112.91(6)	Be-O1	1.552(1)	O3-Be-O3	112.90(7)
Be-O3 (×3)	1.638(1)	O3-Be-O1	105.77(7)	Be-O3 (×3)	1.638(1)	O3-Be-O1	105.78(7)
O3-O3	2.730(1)			O3-O3	2.730(2)		
O3-O1	2.545(2)	O2-B-O3	107.89(5)	O3-O1	2.544(2)	O2-B-O3	108.02(6)
		O2-B-O3′	108.69(5)			O2-B-O3′	108.73(6)
B-O2 (×2)	1.495(1)	O3-B-O3	112.24(8)	B-O2 (×2)	1.496(1)	O3-B-O3	112.05(9)
B-O3 (×2)	1.484(1)	O2-B-O2	111.48(8)	B-O3 (×2)	1.485(1)	O2-B-O2	111.31(9)
O2-O3	2.421(1)			O2-O3	2.423(1)		
O2-O2	2.472(2)			O2-O2	2.470(2)		
O3-O3	2.465(2)			O3-O3	2.464(2)		
Al-O1 (×3)	1.899(2)			Al-O1 (×3)	1.905(2)		
Al-O2 (×3)	1.908(2)			Al-O2 (×3)	1.902(2)		
O1-O1	2.460(3)			O1-O1	2.466(3)		
O2-O2	2.726(2)			O2-O2	2.727(2)		
Cs-O3 (×12)	3.235(1)			Cs-O3 (×12)	3.233(1)		
Al-Al	2.878(5)			Al-Al	2.889(5)		
Cs-Be	3.271(1)			Cs-Be	3.268(1)		

Some of the previous studies on the crystal chemistry of rhodizite reported the presence of hydroxyl groups (Duparc et al. 1911; Donnay et al. 1966, 1967). By contrast, the analysis of our difference-Fourier maps of the nuclear density proves, unambiguously, the absence of hydroxyl groups or water molecules in londonite.

Laurs et al. (2002) reported the occurrence of gem-quality rhodizite-londonite crystals from the Antsongombato pegmatite in the Betafo region, Madagascar. The quality of the stones, their size (dodecahedra that typically measure up to 1 cm, exceptionally up to 6–7 cm), their color (colorless to greenish yellow), and the hardness (8 on the Mohs scale) made the londonites from Antsongombato suitable for jewelry use (Simmons et al. 2001; Laurs et al. 2002). Our interest in londonite rests on its potential use in nuclear applications. The significantly, and unusually, high amount of B_2O_3 (~50 wt%; Table 1) makes the synthetic counterpart of londonite a potential neutron absorber, due to the high capacity of boron to absorb neutrons (the absorption cross-section of boron of "normal" isotopic constitution is 749 ± 4 barns at 2200 m/s; Carter et al. 1953). In addition, the structure of londonite contains Cs and Rb in significant amount (CsO_2+$RbO_2 \geq 8$ wt%; Table 1), making londonite-type materials potential host for nuclear waste. Experiments aimed to describe the thermal, elastic, and chemical stability of londonite are in progress and follow our recent investigations on the stability of other Cs- or B-bearing materials (Gatta et al. 2008a, 2008b, 2009, 2010).

ACKNOWLEDGMENTS

The authors thank the Institut Laue-Langevin, Grenoble, France, for the allocation of neutron beam time. The authors are grateful to Andrea Risplendente and Elena Ferrari for their assistance during the EMPA-WDS and ICP-AES analyses, respectively. The Associate Editor A. Celestian, the Technical Editor R. Peterson, and the reviewers G. Redhammer and R. Skala are thanked for their suggestions.

REFERENCES CITED

Carter, R.S., Palevsky, H., Myers, V.W., and Hughes, D.J. (1953) Thermal neutron absorption cross sections of boron and gold. Physical Review, 92, 716–721.

Coppens, P., Leiserowitz, L., and Rabinovich, D. (1965) Calculation of absorption corrections for camera and diffractometer data. Acta Crystallographica, 18, 1035–1038.

Demartin, F., Diella, V., Gramaccioli, C.M., and Pezzotta, F. (2001) Schiavinatoite, $(Nb,Ta)BO_4$, the Nb analogue of behierite. European Journal of Mineralogy, 13, 159–165.

Donnay, G., Thorpe, A.N., Senftle, F.E., and Sioda, R. (1966) Absence of neutral alkali atoms in rhodizite. Science, 154, 889–890.

Donnay, G., Thorpe, A.N., Sioda, R., and Senftle, F.E. (1967) The formula of rhodizite. Carnegie Institute of Washington Yearbook, 65, 299–300.

Duparc, L., Wunder, M., and Sabot, R. (1911) Contribution à la connaissance des minéraux des pegmatites. Bulletin de la Société Francaise de Minéralogie, 34, 136–139.

Farrugia, L.J. (1999) WinGX suite for small-molecule single-crystal crystallography. Journal of Applied Crystallography, 32, 837–838.

Frondel, C. and Ito, J. (1965) Composition of rhodizite. Tschermaks Mineralogische und Petrographische Mitteilungen, 10, 409–412.

Gatta, G.D., Rotiroti, N., Fisch, M., Kadiyski, M., and Armbruster, T. (2008a) Stability at high-pressure, elastic behaviour and pressure-induced structural evolution of $CsAlSi_5O_{12}$, a potential nuclear waste disposal phase. Physics and Chemistry of Minerals, 35, 521–533.

Gatta, G.D., Rotiroti, N., Zanazzi, P.F., Rieder, M., Drabek, M., Weiss, Z., and Klaska, R. (2008b) Synthesis and crystal structure of the feldspathoid $CsAlSiO_4$: An open-framework silicate and potential nuclear waste disposal phase. American Mineralogist, 93, 988–995.

Gatta, G.D., Rinaldi, R., McIntyre, G.J., Nénert, G., Bellatreccia, F., Guastoni, A., and Della Ventura, G. (2009) On the crystal structure and crystal chemistry of pollucite, $(Cs,Na)_{16}Al_{16}Si_{32}O_{96}\cdot nH_2O$: A natural microporous material of interest in nuclear technology. American Mineralogist, 94, 1560–1568.

Gatta, G.D., Rotiroti, N., Fisch, M., and Armbruster, T. (2010) Stability at high pressure, elastic behaviour, and pressure-induced structural evolution of "Al_5BO_9," a mullite-type ceramic material. Physics and Chemistry of Minerals, 37, 227–236.

Lacroix, A. (1922) Minéralogie de Madagascar 1. Société d'éditions Géographiques, Maritimes et Coloniales, Paris, France.

Larson, A.C. (1967) Inclusion of secondary extinction in least-squares calculations. Acta Crystallographica, 23, 664–665.

Larson, A.C. and Von Dreele, R.B. (1994) General Structure Analysis System (GSAS). Los Alamos National Laboratory Report LAUR 86-748.

Laurs, B.M., Pezzotta, F., Simmons, W.B., Falster, A.U., and Muhlmeister, S. (2002) Rhodizite-londonite from the Antsongombato pegmatite, Central Madagascar. Gems and Gemology, 38, 326–339.

Le Bail, A., Duroy, H., and Fourquet, J.L. (1988) *Ab-initio* structure determination of $LiSbWO_6$ by X-ray powder diffraction. Materials Research Bulletin, 23, 447–452.

Lehmann, M.S., Kuhs, W., McIntyre, G.J., Wilkinson, C., and Allibon, J. (1989) On the use of a small two-dimensional position-sensitive detector in neutron diffraction. Journal of Applied Crystallography, 22, 562–568.

Ouladdiaf, B., Archer, J., McIntyre, G.J., Hewat, A.W., Brau, D., and York, S. (2006) OrientExpress: A new system for Laue neutron diffraction. Physica B, 385–386, 1052–1054.

Pezzotta, F. (2001) Madagascar: A Mineral and Gemstone Paradise. ExtraLapis English no. 1, 97 p. Lapis International, Tuscon, Arizona.

——— (2005) First attempt to the petrogenesis and classification of granitic pegmatites of the Itremo Region (Madagascar). Proceedings of the International Meeting on Crystallization Processes in Granitic Pegmatites, Elba Island (Ialy), May 23–28 (http://www.minsocam.org/MSA/Special/Pig/PIG_articles/PIG_articles.html).

Pring, A., Din, V.K., Jefferson, D.A., and Thomas, J.M. (1986) The crystal chemistry of rhodizite: A re-examination. Mineralogical Magazine, 50, 163–172.

Sears, V.F. (1986) Methods of experimental physics. In K. Sköld and D.L. Price, Eds., Neutron Scattering, 23A, p. 521–550. Academic Press, Orlando.

Sheldrick, G.M. (1997) SHELX-97. Programs for crystal structure determination and refinement. University of Göttingen, Germany.

Simmons, W.B., Pezzotta, F., Falster, A.U., and Webber, K.L. (2001) Londonite, a new mineral species: The Cs-dominant analogue of rhodizite from the Antandrokomby granitic pegmatite, Madagascar. Canadian Mineralogist, 39, 747–755.

Strunz, H. (1938) Gitterkonstante und Raumgruppe von Rhodizit. Naturwissenschaften, 26, 217.

Taxer, K.J. and Buerger, M.J. (1967) The crystal struture of rhodizite. Zeitschrift für Kristallographie, 125, 423–436.

Wilkinson, C., Khamis, H.W., Stansfield, R.F.D., and McIntyre, G.J. (1988) Integration of single-crystal reflections using area multidetectors. Journal of Applied Crystallography, 21, 471–478.

Manuscript received March 16, 2010
Manuscript accepted June 3, 2010
Manuscript handled by Aaron Celestian