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Single-crystal structure refinement of synthetic ^{M4}K-substituted potassic richterite, $K(KCa)Mg_5Si_8O_{22}(OH)_2$

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ABSTRACT

The crystal structure of a potassic richterite, $K(KCa)Mg_5Si_8O_{22}(OH)_2$ synthesized at 15 GPa and 1400 °C, was refined from single-crystal X-ray diffraction data. The unit-cell parameters are: a = 10.1926(5), b = 18.1209(3), c = 5.2736(2) Å, and β = 105.514(5)°. The refinement shows that the M4 site is occupied by K and Ca at a ratio of 1:1 with no site splitting. Entrance of K into the M4 site mainly affects the local environment: the M4-O2, M4-O4, and M4-O6 bond lengths in KK richterite are 3.4, 3.7, and 3.1% longer, respectively, than the corresponding ones in potassium richterite, whereas the M4-O5 distance is 1.2% shorter, giving rise to a more regular M4 polyhedron. Three major structural adjustments allow the M4 site to accommodate large K: a shift of the M4 cation along the two-fold b axis, a modification of the double silicate-chain configurations, and relative displacements of the two back-to-back tetrahedral chains. K at the A site is completely ordered at the Am position. The average of eight shortest A-O distances is 0.044 Å longer than that in potassium richterite, despite the A site being fully filled with K in both structures. The unpolarized Raman spectrum displays only one single band at 3735.5 cm^{-1} in the OH-stretching region.

INTRODUCTION

Based on natural occurrence and experimental evidence, potassium-richterite is a potential host for water and alkali elements in the Earth's upper mantle to a depth of at least 400 to 450 km (Dawson and Smith 1977; Erlank et al. 1987; Sudo and Tatsumi 1990; Foley 1991; Luth 1997; Inoue et al. 1998). Its upper pressure stability limit thus exceeds that of any other hydrous silicate known from natural rocks. Above ~10 GPa and in the presence of water, potassium richterite is presumably the primary reservoir for K and Rb in peridotitic mantle rocks. The crystal structure of potassium richterite was refined from single-crystal X-ray diffraction data by Papike et al. (1969), Cameron et al. (1983), and Oberti et al. (1992). In addition, many powder X-ray structure refinements exist on various synthetic potassium richterites (Gottschalk and Andrut 1998 and references therein).

Natural potassium richterites are close to the end-member composition $KNaCaMg_5Si_8O_{22}(OH)_2$ (Dawson and Smith 1977; Erlank et al. 1987) with K ≈1.0 apfu. High-pressure experiments (Sudo and Tatsumi 1990; Luth 1997; Inoue et al. 1998; Konzett et al. 1997), however, have produced potassium richterites with K up to 1.95 apfu, which suggests the presence of a significant amount of K in the M4 site of the amphibole structure, a crystallographic position that has been considered to be too small to accommodate such a large cation (Papike et al. 1969). Unit-cell parameters of a potassium richterite with the composition $K_{1.95}Ca_{1.05}Mg_5Si_8O_{22}(OH)_2$ were determined by Inoue et al. (1998) using powder X-ray diffraction. Here, we present results of a single-crystal X-ray diffraction study on a synthetic potassic richterite, $K_2CaMg_5Si_8O_{22}(OH)_2$, in which the M4 site is filled with K and Ca at a ratio of 1:1, to characterize the effects of K at the M4 site on the structure. We designate our sample KK richterite for simplicity and to distinguish it from potassium richterite.

EXPERIMENTAL PROCEDURES

The sample synthesized was at 15 GPa and 1400 °C for 5 h using a multi-anvil apparatus. The starting material was a mixture of high purity (99.95%) K_2CO_3, $CaCO_3$, $Mg(OH)_2$, and SiO_2 of stoichiometric $K_2CaMg_5Si_8O_{22}(OH)_2$ composition. After decarbonation by step-heating the starting material was sealed into a Pt_{100} capsule. The KK richterite coexists with its breakdown products clinopyroxene, clinoenstatite and wadeite-structure $K_2Si_4O_9$ (Inoue et al. 1998) and forms blocky, subhedral crystals up to ~100 x 60 x 50 μm in size. After the synthesis, the Pt-capsule was embedded in epoxy resin, ground to expose the center of the charge and polished for electron microprobe analysis. Analytical conditions were 15 kV, 20 nA, and a 20 μm raster beam size. Natural orthoclase and wollastonite, synthetic MgO and SiO_2 were used as standards. The average composition (9 points) based on 23 O atoms and stoichiometric OH is $K_{2.07\pm0.01}Ca_{0.97\pm0.03}Mg_{4.99\pm0.02}Si_{8.00\pm0.01}O_{22}(OH)_2$. A single-crystal fragment (0.09 mm × 0.06 mm × 0.04 mm), extracted from a polished mount, was chosen for further X-ray study based on optical examination, precession photography, and X-ray diffraction peak profiles. A Picker four-circle diffractometer equipped with a Mo X-ray tube (β-filtered) was employed for all X-ray diffraction measurements. Unit-cell parameters were determined by fitting the positions of 20 reflections with $20° < 2\theta < 35°$

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TABLE 1. Atomic coordinates and displacement parameters of synthetic ^{M4}K-substituted potassic richterite

Atom	*x*	*y*	*z*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	$\beta_{eq.}$
M1	0	0.0889(1)	0.5	0.0014(2)	0.0005(0)	0.0052(6)	0	0.0001(3)	0	0.59(3)
M2	0	0.1800(1)	0	0.0018(2)	0.0004(0)	0.0070(6)	0	0.0008(3)	0	0.66(3)
M3	0	0	0	0.0010(2)	0.0004(1)	0.0049(8)	0	0.0004(4)	0	0.50(4)
M4	0	0.2819(1)	0.5	0.0027(1)	0.0007(0)	0.0113(4)	0	0.0025(2)	0	0.99(3)
T1	0.2706(1)	0.0847(1)	0.3065(2)	0.0012(1)	0.0004(0)	0.0039(3)	0.0000(1)	0.0001(1)	-0.0002(1)	0.49(2)
T2	0.2812(1)	0.1708(1)	0.8131(2)	0.0014(1)	0.0004(0)	0.0040(3)	-0.0002(0)	-0.0003(1)	-0.0001(1)	0.54(2)
O1	0.1083(3)	0.0869(1)	0.2204(5)	0.0015(2)	0.0004(1)	0.0041(9)	-0.0001(1)	0.0001(4)	-0.0001(2)	0.64(5)
O2	0.1175(3)	0.1689(1)	0.7298(5)	0.0017(2)	0.0009(1)	0.0072(10)	-0.0001(1)	0.0002(4)	-0.0005(2)	0.89(5)
O3	0.1038(4)	0	0.7188(7)	0.0017(3)	0.0005(1)	0.0073(13)	0	0.0007(6)	0	0.71(7)
O4	0.3589(3)	0.2463(2)	0.8088(6)	0.0043(3)	0.0007(1)	0.0100(11)	-0.0010(1)	-0.0011(4)	-0.0001(2)	1.30(6)
O5	0.3399(3)	0.1289(1)	0.1057(5)	0.0017(2)	0.0008(1)	0.0051(9)	0.0001(1)	0.0002(4)	0.0007(2)	0.75(5)
O6	0.3339(3)	0.1145(1)	0.6050(5)	0.0023(3)	0.0007(1)	0.0046(9)	-0.0001(1)	-0.0008(4)	-0.0007(2)	0.84(5)
O7	0.3271(4)	0	0.3047(8)	0.0016(3)	0.0004(1)	0.0117(14)	0	0.0005(6)	0	0.81(7)
Am	0.013(1)	0.5	0.028(3)	0.0004(9)	0.0015(1)	0.0119(39)	0	-0.0006(11)	0	1.18(7)
H	0.202(7)	0	0.747(14)							1.3(8)

TABLE 2. Selected interatomic distances (Å) in synthetic ^{M4}K-substituted potassic richterite

M1-O1 (×2)	2.065(3)	T1-O1	1.595(3)
M1-O2 (×2)	2.056(3)	T1-O5	1.632(3)
M1-O3 (×2)	2.096(3)	T1-O6	1.626(3)
Avg.	2.072	T1-O7	1.640(2)
		Avg.	1.623
M2-O1 (×2)	2.175(3)		
M2-O2 (×2)	2.102(3)	T2-O2	1.608(3)
M2-O4 (×2)	2.023(4)	T2-O4	1.584(4)
Avg.	2.100	T2-O5	1.680(3)
		T2-O6	1.688(3)
M3-O1 (×4)	2.089(2)	Avg.	1.640
M3-O3 (×2)	2.039(4)		
Avg.	2.072	Am-O5 (×2)	2.958(8)
		Am-O5 (×2)	3.023(8)
M4-O2 (×2)	2.514(3)	Am-O6 (×2)	2.977(10)
M4-O4 (×2)	2.497(3)	Am-O6 (×2)	3.232(10)
M4-O5 (×2)	2.790(3)	Am-O7	2.687(13)
M4-O6 (×2)	2.683(3)	Am-O7	2.692(13)
Avg.	2.621	Am-O7	3.460(14)
		Am-O7	3.779(14)
		Avg. of 8	2.912
		Avg. of 12	3.083

following the procedure of King and Finger (1979), yielding a = 10.1926(5), b = 18.1209(3), c = 5.2736(2) Å, β = 105.514(5)°, and V = 938.53(6) Å^3. These values differ slightly from those determined by Inoue et al. (1998) using powder X-ray diffraction: a = 10.180(8), β = 18.078(12), c = 5.285(6) Å, b = 105.17(8)°, and V = 938.7(14) Å^3. The significantly smaller b dimension and large uncertainty measured by Inoue et al. (1998) could be due to the mis-indexing of some powder lines used for the unit-cell parameter refinement.

X-ray diffraction intensity data from one quadrant of reciprocal space with 0° ≤ 2θ ≤ 60° were collected on the basis of the C-centered lattice using ω scans of 1° width in step increments of 0.025° and 2 s per step counting time. To check if any reflections violated the $C2/m$ symmetry, a data set with 0° ≤ 2θ ≤ 30° was first collected in a 1 s per step counting time based on the primitive lattice; no such reflections were detected. Digitized step data were integrated by the method of Lehmann and Larsen (1974) with background manually reset when necessary. Corrections were made for Lorentz and polarization effects, and for X-ray absorption by the crystal (μ = 15.64 cm^{-1}). Reflections having intensities greater than 2σ(I) were considered as observed and included in the refinement. There are total 1064 observed reflections out of 1538 measured ones.

In all refinements, the T1 and T2 sites were assumed to be fully occupied by Si, the M1, M2, and M3 sites by Mg, the M4 site by (Ca + K), and the A site by K. The ratio of Ca/K at the M4 site was allowed to vary during the refinements and the amount of K at the A site was constrained to that occupying the M4 site for charge balance. The initial structural model with space group $C2/m$ was taken from Robert et al. (1993) with the A-site K assigned at the Am position, as suggested by Boschmann et al. (1994) and Hawthorne et al. (1996). Procedures of structure refinements are similar to those described by Yang et al. (1997). The anisotropic refinement for all atoms converged after five cycles, giving R_w = 4.8 and R = 4.4%. No significant peaks were revealed in difference Fourier maps at convergence of the refinement except for a slightly positive peak for the H position at (~0.2, 0, ~0.7). The total refined K content was 1.98(2) apfu, in agreement with the microprobe analysis. Hence, with given experimental uncertainties, K can be considered to be completely ordered at the Am position. A split M4-site model was rejected because it failed to converge after 15 cycles of refinements and resulted in negative displacement factors for some atoms. Final atomic coordinates and displacement parameters are presented in Table 1 and selected interatomic distances in Table 2.

Raman spectra were recorded with a Dilor XY confocal microRaman spectrometer equipped with a cryogenic Wright Model CCD detector. The excitation source was the 514 nm line of a Coherent Innova Model 90-5 Ar+ laser operating at 150 mW with an integration time of 600 s.

RESULTS AND DISCUSSION

The most obvious difference between the K- and KK-richterite structures is in the bonding environments around the M4 cation. In potassium richterite, the M4 site has a (6 + 2) coordination (Papike et al. 1969): six O atoms (two O2, two O4, and two O6) at an average distance of 2.479 Å, and two (O5) at 2.825 Å. With the replacement of Na by K, the M4-O2, M4-O4, and M4-O6 distances in KK richterite are 3.4, 3.7, and 3.1% longer, respectively, than the corresponding ones in potassium richterite, whereas the M4-O5 distance (2.790 Å) is 1.2% shorter than that in potassium richterite. Thus, the substitution of K for Na at the M4 site significantly reduces the differences among individual M4-O bond lengths, creating a more evenly spatially distributed M4-cation bond valence. As increasing pressure tends to reduce the bond-length differences within a polyhedron, the configuration of the M4 site in KK richterite is likely more favored by high pressure than that in potassium richterite, which may be responsible in part for its large pressure stability.

Compared to the potassium richterite structure, three major structural adjustments are required to accommodate the large K cation at the M4 site in KK richterite: (1) a shift of the M4 cation along the two-fold b axis (x and z positions being fixed by the $C2/m$ symmetry), (2) a modification in the configuration of the double silicate chains, and (3) relative displacements of the two back-to-back tetrahedral chains. Relative to the M4-cation position in potassium richterite ($y = 0.2779$), that in KK richterite ($y = 0.2819$) is displaced considerably away from the octahedral bands formed by M1, M2, and M3, as evidenced by the observed increase in the M4-O2 and M4-O4 bond lengths. Examination of structural data available for various amphiboles indicates that such a shift of the M4-cation position is necessary for minimizing the octahedral band distortion that may be caused by the introduction of large cations into the M4 site. The response of the silicate-chain configuration to the entry of K at the M4-site is manifested in the increase of its kinking and bowing, the former being defined by the O5-O6-O5 angle and the latter by the O4-O7-O4 angle projected onto the a^*-b plane (Fig. 1a). The O5-O6-O5 angle is 170.2(2)° in potassium richterite, whereas it is 168.4(1) in KK richterite. The increased chain kinking in KK richterite moves the O6 atom farther away from and O5 closer to the M4 cation, accounting in part for the longer M4-O6 and the shorter M4-O5 distances in KK richterite. The presence of K at the M4 site also increases the bowing of the double chains in KK richterite by 1.1° relative to that in potassium richterite. Associated with the increased bowing is the increase in the I-beam thickness (the O4-O4′ distance in Fig. 1b) from 6.993 Å in potassium richterite to 7.050 Å in KK richterite.

Between the two back-to-back double tetrahedral chains, two types of relative displacements result from the replacement of Na by K at the M4 site, one along $\mathbf{c}$ and the other along $\mathbf{a}^*$. The relative displacement along $\mathbf{c}$ can be measured in terms of the chain displacement factor (CDF), which is defined by the distance between the centers of the two opposing six-membered tetrahedral rings (Sueno et al. 1973). As demonstrated by Sueno et al. (1973), this value decreases with increasing the M4 cation size, ranging from 0.3020 for ferromagnesian clinoamphiboles to 0.1762 for potassium richterite. The CDF value we obtained for KK richterite is 0.1511, the smallest value found in amphiboles thus far. This relative chain displacement, together with the increased kinking of the silicate chains, accounts for the observed decrease in the M4-O5 bond length and is also consistent with the β angle being larger in KK richterite. The relative displacement along $\mathbf{a}^*$ enlarges the separation between the two back-to-back silicate chains and can be measured by the O4-O4′ and O7-O7′ distances projected onto the a^*-b plane (Fig. 1b) (Comodi et al. 1992). These two values are 2.685 and 3.225 Å in potassium richterite, respectively, whereas they are 2.772 and 3.395 Å in KK richterite. The enlarged separation between the two back-to-back double chains in KK richterite is probably correlated to the change in the configuration of silicate chains because it could help reduce the strain induced by the increased bowing.

Another noticeable feature of the KK richterite structure is that, owing to a strong local charge imbalance on the O4 site, O4 exhibits the greatest isotropic displacement factor of all oxygen atoms (Table 1) and the most anisotropic vibrational ellipsoid, with the largest displacement vector aligned approximately along the M4-O4 bond. This situation could be improved by a split (M4 + M4′) site as smaller divalent cations would preferentially enter the more tightly coordinated M4′ site that is closer to O4 to achieve a high bond-valence value for O4. In this sense, substitution of smaller Mg^{2+} or Fe^{2+} for Ca^{2+} would enhance the site splitting and thus should be favored energetically by the KK richterite structure. It is noteworthy that a similar mechanism has been proposed by Harlow (1996) for K-rich diopside. According to Harlow (1996), providing that the charge balance can be maintained, substitution of smaller Mg^{2+} and/or Fe^{2+} for Ca^{2+} in the M2 site in diopside would facilitate the K uptake, because the strain produced by the entrance of K into the large M2 site may be compensated for by a split (M2 + M2′) site resulting from the large size difference between K^+ and Mg^{2+}/Fe^{2+} ionic radii.

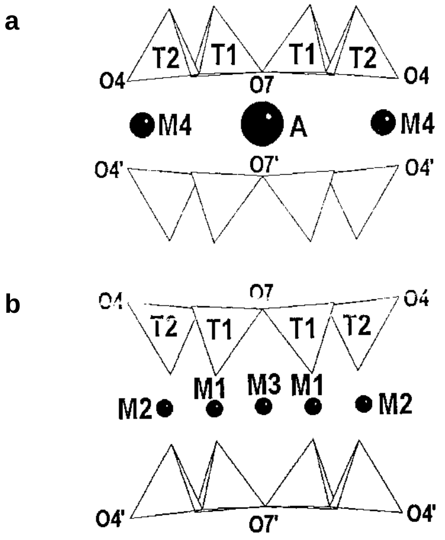

FIGURE 1. The KK richterite structure projected along [001]: **(a)** showing the configuration of the two back-to-back double tetrahedral chains and **(b)** showing the configuration of the I-beam.

Cation disorder at the A site in amphiboles has been a subject of many experimental studies (see Hawthorne 1983 for a review). X-ray structure refinements have shown that K prefers to order at the Am site, whereas Na may display a complex pattern of positional disorder (e.g., Boschmann et al. 1994; Hawthorne et al. 1996). Our data are consistent with previous studies. Nevertheless, owing to the enlarged separation between the two back-to-back silicate chains and the increased bowing of double chains, the average of eight shortest A-O distances in KK richterite is 0.044 Å longer than that in potassium richterite (Papike et al. 1969), despite the A site being fully filled with K in both structures.

In an infrared spectroscopic study on synthetic richterites in the KNCMSH(F) system, Robert et al. (1989) found a high-intensity band consisting of two split components at 3735 and 3730 cm^{-1} along with a minor band at 3670 cm^{-1}. These authors interpreted the 3670 cm^{-1} tremolite-type band as a result of a partially vacant A-site, and the splitting of the high-intensity band in terms of a positional disorder of K at the Am and A2/*m*

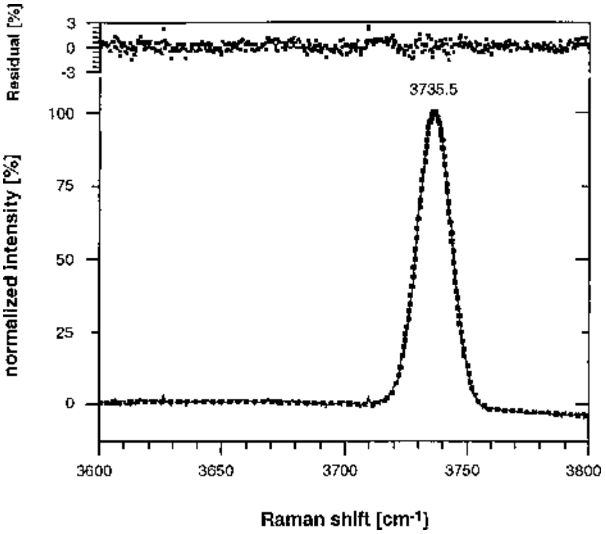

FIGURE 2. Raman spectrum of synthetic KK richterite in the OH-stretching region. Note that the Raman data (dots) can be perfectly fitted by a single peak (full line).

sites. A similar band configuration was observed by Della Ventura and Robert (1990) for synthetic sodic strontium richterite $Na(NaSr)Mg_5Si_8O_{22}(OH)_2$, but not for potassic strontium richterite $K(NaSr)Mg_5Si_8O_{22}(OH)_2$, which showed neither the tremolite-type band nor the high-intensity OH-band splitting at 3735 cm^{-1}. This observation led them to suggest a fully occupied A-site with K ordered at the central A2/*m* position in potassic strontium richterite. Gottschalk and Andrut (1998) studied synthetic (K,Na)-richterites with variable A-site vacancies and did not observe any splitting of the main IR band in the region 3730-3735 cm^{-1}. The unoriented Raman spectra in the OH-stretching region (3500-3900 cm^{-1}) collected from several KK richterite crystals, including the one used for the X-ray data measurements, exhibits a sharp band at 3735.5 cm^{-1} (Fig. 2) which can be fitted by a single symmetric Gaussian band (Della Ventura et al. 1996), a result consistent with FTIR results obtained by Gottschalk and Andrut (1998) for (K,Na)-richterite. This spectrum is similar to the one measured for potassium strontium richterite by Della Ventura and Robert (1990). It is unclear whether the Raman spectra in OH-stretching are directly comparable to the infrared spectra; however, our Raman spectrum (Fig. 2) suggests that the interpretation of Della Ventura and Robert (1990) is probably incorrect, since the single-crystal refinement clearly shows that K is completely ordered at the Am position in KK richterite. Some of these uncertainties regarding positional disorder of cations at the A site need more systematic studies on different amphibole compositions by combining structure refinements with spectroscopic measurements

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