LETTER

Crystal growth and structure of $K_2Al_2Si_3O_{10} \cdot KCl$: A new anhydrous zeolite-type phase with the edingtonite framework

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Abstract

Single crystals of $K_2Al_2Si_3O_{10} \cdot KCl$, a new anhydrous zeolite-type phase, were grown by a hydrothermal flux technique. This compound is tetragonal, $P\bar{4}2_1m$, $a = 9.755(1)$ Å, $c = 6.488(1)$ Å, Z = 2. The structure refinement ($R = 0.056$, 978 reflections) shows considerable Al/Si disorder at T(1) and T(2) sites. The K^+ and Cl^- ions occur in two types of channels parallel to [001] and $\langle 110 \rangle$ within an aluminosilicate framework, identical to that found in edingtonite, $BaAl_2Si_3O_{10} \cdot (4 - x)H_2O$.

Introduction

Among the aluminosilicate minerals with framework structures there are a few known examples, such as sodalite, $3NaAlSiO_4 \cdot NaCl$, and scapolite, $3NaAlSi_3O_8 \cdot NaCl$ and $3CaAl_2Si_2O_8 \cdot CaCl_2$, in which the alkali (or alkaline-earth) and halide ions occur in open channels. Because of their anhydrous nature, they are not classified as zeolites in spite of their zeolite-type aluminosilicate frameworks. In sodalite, the Cl^- ion can be replaced by an $(OH)^-$ group. However, zeolite analogues of these phases containing water molecules are unknown. In this letter we report the synthesis and crystal structure of a new anhydrous zeolite-type phase: $K_2Al_2Si_3O_{10} \cdot KCl$ with the aluminosilicate framework of the zeolite edingtonite, $BaAl_2Si_3O_{10} \cdot (4 - x)$-$H_2O$. To our knowledge, this is the first example of an anhydrous halide-bearing phase with a zeolite analogue.

Crystal growth

The new $K_2Al_2Si_3O_{10} \cdot KCl$ phase was synthesized by the hydrothermal flux method during an attempt to grow single crystals of tetragonal leucite, $KAlSi_2O_6$, below the temperature of transition from tetragonal to cubic leucite (~ 625 °C). The charge consisted of ~ 34 wt% powdered natural leucite (nearly pure $KAlSi_2O_6$ from a site near Rome, Italy) and ~ 66 wt% of a eutectic mixture of KCl (~ 34 wt%), KF (~ 23 wt%) and K_2CO_3 (~ 43 wt%). No water was added, but the adsorbed H_2O content may be 1–2 wt%. The charge was loaded in a cold-seal pressure vessel at 5000 psi Ar-pressure and 570 °C ± 5 for 17 d. The temperature was raised to 600 °C for 0.5 h and slowly cooled to 500 °C over 5 d. After cooling, the charge was crushed and washed with H_2O, which yielded a large number of glass-clear tetragonal prismatic crystals about 0.1–0.15 mm in size. The crystals were originally believed to be tetragonal leucite, but single crystal X-ray precession photographs indicated that they represent a new phase. X-ray wavelength scans using the electron microprobe indicated the presence of Cl in addition to K, Al, and Si. The microprobe analysis (avg. of 6 points) Si 6.141, Al 3.880, K 5.965, Cl 2.173, and O 20.00 gives the stoichiometric chemical formula $2[K_2Al_2Si_3O_{10} \cdot KCl]$.

Crystal data and structure determination

Single-crystal X-ray rotation and precession photographs show tetragonal symmetry with $a \sim 9.76$ Å and $c \sim 6.50$ Å. A single crystal (0.12 × 0.12 × 0.15 mm) was mounted on an automatic single-crystal X-ray diffractometer with $MoK\alpha$ radiation monochromatized by reflection from a graphite crystal. Unit-cell dimensions were determined by least-squares refinement of 2θ values of 25 reflections ($30° < 2\theta < 45°$) (Table 1). The observed extinction conditions ($h00$, $h = 2n$) indicate two possible space groups: $P\bar{4}2_1m$ and $P42_12$, the former being the correct one, as confirmed by the structure determination. The intensities of all hkl reflections ($2\theta \leq 65°$) were measured by the ω-2θ scan method using monochromatized $MoK\alpha$ radiation and a scan rate of 3° per min. The X-ray diffraction peaks were unusually broad, indicating considerable mosaic spread. Out of a total of 1204 hkl reflections, 978 were $>3\sigma(I)$, where $\sigma(I)$ is the measured standard deviation.

The structure determination was initiated by direct methods using the program Multan and the space group

TABLE 1. K₂Al₂Si₃O₁₀·KCl: Crystal data

	K₂Al₂Si₃O₁₀·KCl Colorless tetragonal prisms	
Tetragonal, $\bar{4}2m$		
a (Å):	9.7553(9)	Size of crystal (mm): 0.12 × 0.12 × 0.15
c (Å):	6.4877(6)	μ(MoKα): 17.811
V (Å³):	617.41	Total no. of refl.: 1204
Z:	2	No. of refl. >3σ(I): 978
Space group:	$P\bar{4}2_1m$	R: 0.056
ΛMoKα (Å):	0.71069	R_w: 0.049
D_c (g/cm³):	2.44	

TABLE 2B. Anisotropic thermal parameters, β_{ij}(×10⁴)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
T(1)	31(2)	21(2)	42(6)	0	0	0
T(2)	29(1)	30(1)	50(2)	−5(1)	−4(1)	2(1)
Cl	148(5)	148(5)	156(10)	46(6)	0	0
K(1)	65(2)	65(2)	172(8)	24(2)	0	0
K(2)	152(3)	152	88(4)	−106(3)	12(3)	−12
O(1)	42(3)	42	105(11)	6(4)	−7(5)	7
O(2)	43(3)	54(4)	70(7)	−1(3)	−1(5)	4(5)
O(3)	51(4)	45(3)	81(7)	−12(3)	8(5)	−1(5)

Note: Form of the anisotropic temperature factors, β_{ij},
$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.
Standard deviations of the last digit are in parentheses.

$P\bar{4}2_1m$. The heavy-atom positions (K, Cl, Si, Al) were determined from the E maps and subsequently confirmed from interatomic vectors in Patterson maps. Structure-factor calculations followed by Fourier and difference Fourier syntheses yielded the O atom locations. The structure was refined by full matrix least-squares methods (RFINE 4, Finger and Prince, 1975) using anisotropic temperature factors and a unit-weighting scheme. The atomic scattering factors with anomalous dispersion for K, Al, Si, O and Cl were taken from *International Tables for X-ray Crystallography,* vol. IV (1974). Site-occupancy refinement indicated slight deficiencies at K(1) and Cl positions. The final R-factor for 978 observed reflections is 0.056 ($R_w = 0.049$).

The tetragonal structure so determined implied extensive Al/Si disorder in the tetrahedral sites. To check the possibility of an ordered structure with orthorhombic symmetry, the structure was also refined in the space group $P2_12_12$ (cf. edingtonite: Galli, 1976; Kvick and Smith, 1983). However, nearly identical a and b dimensions and T-O bond lengths similar to those of the earlier refinement indicated the true symmetry to be tetragonal ($P\bar{4}2_1m$). The atomic positional and thermal parameters with standard deviations are listed in Table 2, interatomic distances and angles in Table 3, and a list of observed and calculated structure factors in Table 4.[1]

[1] A copy of Table 4 may be ordered as Document AM-90-435 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC, 20036, U.S.A. Please remit $5.00 in advance for the microfiche.

DESCRIPTION OF THE STRUCTURE AND CRYSTAL CHEMICAL RELATIONS WITH EDINGTONITE

The aluminosilicate framework of K₂Al₂Si₃O₁₀·KCl is identical with that of tetragonal edingtonite (space group $P\bar{4}2_1m$) (Mazzi et al., 1984). It consists of natrolite-type 4-1 aluminosilicate chains parallel to c cross-connected to four such adjacent chains by sharing tetrahedral corners, resulting in a four-connected, three-dimensional framework (Fig. 1). Each single chain consists of a central Al,Si (T1) tetrahedron, four corners of which are shared with four other (Al,Si) (T2) tetrahedra. Within the framework, two types of octagonal channels are formed parallel to [001] and ⟨110⟩, bounded by near-circular, eight-membered tetrahedral rings. There are also four-membered tetrahedral rings at each corner of the *ab* projection of the unit cell (Fig. 1). Alternating K(1) and Cl atoms form linear chains within the nonintersecting channels parallel to [001] whereas alternating K(2) and Cl atoms form zigzag chains within the intersecting channels parallel to ⟨110⟩.

There are two distinct (Al,Si) tetrahedra; T(1) with point symmetry $\bar{4}(S_4)$ [avg. T(1)-O 1.635(4) Å] is considerably enriched in Si compared to T(2) with point symmetry $1(C_1)$ [avg. T(2)-O 1.675(4) Å]. If the intrinsic Si-O and Al-O distances at T(1) and T(2) sites are assumed to be 1.617 and 1.743 Å, respectively (cf. Al/Si-ordered edingtonite, Kvick and Smith, 1983), approximate site occupancies are T(1) 0.20 Al, 0.80 Si and T(2) 0.45 Al, 0.55 Si. The degree of Al/Si disorder in two natural tetragonal edingtonites is much higher as shown by average T(1)-O

TABLE 2A. Atomic positional and equivalent isotropic thermal parameters

Atom	Wyckoff position	Site occ.	x	y	z	B_{eq}
T(1)	2(a)	1	0	0	0	1.05(8)
T(2)	8(f)	1	0.1524(1)	0.1157(1)	0.6213(2)	1.02(4)
Cl	2(c)	0.98(1)	1/2	0	0.0478(7)	4.43(24)
K(1)	2(c)	0.98(1)	1/2	0	0.5450(5)	2.49(13)
K(2)	4(e)	1.0000(7)	0.2598(3)	0.2402	0.1226(4)	3.29(11)
O(1)	4(e)	1	0.2985(3)	0.2015	0.6234(10)	1.18(14)
O(2)	8(f)	1	0.0445(4)	0.1900(4)	0.4524(5)	1.55(12)
O(3)	8(f)	1	0.0818(4)	0.1123(4)	0.8589(6)	1.60(12)

Note: Standard deviations of the last digits are in parentheses.

TABLE 3. $K_2Al_2Si_3O_{10} \cdot KCl$: Interatomic distances (Å) and angles (°)

K polyhedron			
K1-O(1) (×2)	2.827(5)	K2-O(1)	3.293(7)
-O(2) (×4)	3.056(4)	-O(1')	3.282(7)
-Cl	3.226(6)	-O(2) (×2)	3.038(4)
-Cl'	3.262(6)	-O(3) (×2)	2.739(4)
		-O(3') (×2)	3.457(4)
Mean K(1)-O	2.980	-Cl	3.350(4)
Mean K(1)-Cl	3.244	-Cl'	3.750(4)
		Mean K(2)-O	3.130
		Mean K(2)-Cl	3.550
Cl octahedron			
Cl-K(1)	3.262(6)		
-K(1')	3.226(6)		
-K(2) (×2)	3.350(4)		
-K(2') (×2)	3.750(4)		
Mean	3.448		
T(1) tetrahedron			
T(1)-O(1) (×4)	1.635(4)	O(3)-O(3')	2.711(7)	111.9(3)
Mean	1.635	-O(3'')	2.651(6)	108.3(1)
		-O(3''')	2.651(6)	108.3(1)
T(2) tetrahedron			
T(2)-O(1)	1.653(2)	O(1)-O(2)	2.716(5)	109.0(2)
-O(2)	1.683(4)	-O(2')	2.669(4)	106.6(2)
-O(2')	1.675(4)	-O(3)	2.750(5)	110.7(2)
-O(3)	1.688(4)	O(2)-O(2')	2.762(6)	110.7(2)
Mean	1.675	-O(3)	2.768(5)	110.3(2)
		O(2')-O(3)	2.745(5)	109.4(2)
T(1)-T(2)	3.085(1)	T(1)-O(3)-T(2)		136.3(2)
T(1)-T(2')	3.073(2)	T(2)-O(2)-T(2')		132.4(3)
T(2)-T(2')	3.199(3)	T(2)-O(1)-T(2')		180.9(4)

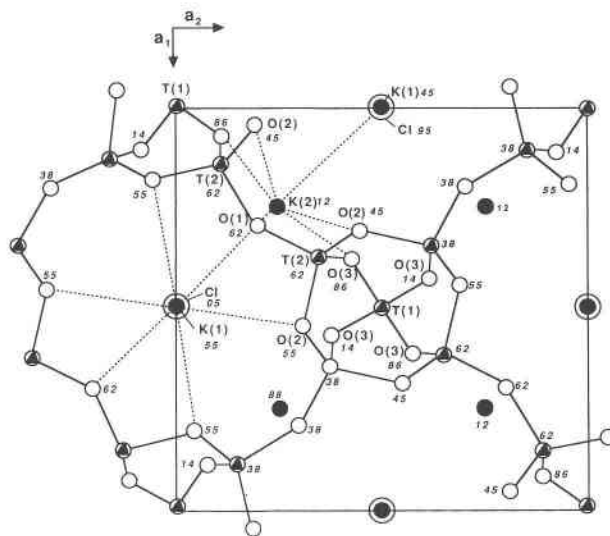*Note:* For interatomic angles, read O(3)-T(1)-O(3'), etc. Standard deviations of the last digit are in parentheses.

Fig. 1. Projection of the $K_2Al_2Si_3O_{10} \cdot KCl$ structure down the c axis. The z-coordinates are shown by double-digit numbers next to each atom.

and T(2)-O distances of 1.658 (1.660) and 1.668 (1.666) Å, respectively (Mazzi et al., 1984). The existence of the Al/Si ordered orthorhombic phase of edingtonite points to the possibility of a similar orthorhombic phase of $K_2Al_2Si_3O_{10} \cdot KCl$, which is yet to be found.

Both K(1) and K(2) polyhedra are hexagonal bipyramids, where the hexagonal plane consists of six O atoms from the eight-membered rings and two Cl atoms form the apices. The $K(1)O_6Cl_2$ polyhedron with point symmetry $mm2(C_{2v})$ is more regular, the hexagonal plane being slightly distorted and the two K(1)-Cl distances being nearly equal [3.226(6) and 3.262(6) Å]. In contrast, the hexagonal plane in the $[K(2)O_6Cl_2]$ polyhedron with point symmetry 1 (C_1) is highly puckered (boat-shaped) and the two K(2)-Cl distances are quite different [3.350(4) and 3.750(4) Å].

Cl has a sixfold octahedral coordination with an average Cl-K distance of 3.448(5) Å, which is considerably larger than that in KCl (3.15 Å). The $[ClK_6]$ octahedron with point symmetry $mm2(C_{2v})$ consists of four K(2) atoms in a rectangular plane with two K(1) atoms forming the apices. As mentioned earlier, a set of nonintersecting K(1)-Cl-K(1)... chains is parallel to c. Another set of intersecting K(2)-Cl-K(2)... chains is parallel to ⟨110⟩.

A comparison of this structure with that of edingtonite shows that the K(1) position corresponds to the Ba position, whereas the K(2) position corresponds to one of the two H_2O molecules (W1) in tetragonal edingtonite (Mazzi et al., 1984). The replacement of the Ba^{2+} ion in

edingtonite requires two K^+ ions for charge balance. Hence, the K^+ ions in the K(2) position in $K_2Al_2Si_3O_{10} \cdot KCl$ should be considered as the ones required for the Ba^{2+} replacement. It is interesting to note that the site-occupancy refinement indicates full occupancy at the K(2) site, whereas slight deficiencies were found at the K(1) and Cl positions. The nonstoichiometry along the charge-balanced K^+-Cl^--K^+... chains parallel to the c axis, if real, apparently does not affect the structural stability. This situation is comparable to the nonstoichiometry with respect to H_2O molecules in zeolites.

CONCLUSION

The preparation and characterization of $K_2Al_2Si_3O_{10} \cdot KCl$ as an anhydrous halide-bearing structural analogue of the zeolite edingtonite, $BaAl_2Si_3O_{10} \cdot (4 - x)H_2O$, point to the interesting possibility of the synthesis of a whole new series of anhydrous zeolite-type compounds stuffed with extra alkali and halide ions instead of H_2O molecules.

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