

CELL EDGES AND INFRARED SPECTRA OF SYNTHETIC LEUCITES AND POLLUCITES IN THE SYSTEM KAlSi_2O_6 — $\text{RbAlSi}_2\text{O}_6$ — $\text{CsAlSi}_2\text{O}_6$

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ABSTRACT

Cell parameters and infrared-absorption data are presented to document the structural changes that occur when a larger monovalent cation replaces a smaller one in leucites and pollucites of the system KAlSi_2O_6 — $\text{RbAlSi}_2\text{O}_6$ — $\text{CsAlSi}_2\text{O}_6$, synthesized at $P(\text{H}_2\text{O}) = 1$ kbar, $T = 600^\circ\text{C}$. These changes parallel those experienced by the structures upon heating. A first-order break is found along the joins $\text{RbAlSi}_2\text{O}_6$ — $\text{CsAlSi}_2\text{O}_6$ and KAlSi_2O_6 — $\text{CsAlSi}_2\text{O}_6$ at room temperature, near 45 and 67 mol % respectively. In binary T - X sections, and by analogy, inside the ternary system, this first-order break may represent a two-phase loop, true displacive transformations being restricted to end-member compositions.

INTRODUCTION

A number of leucites and pollucites have been synthesized as part of a study of partition coefficients governing the distribution of a monovalent cation $X(\text{K},\text{Rb},\text{Cs})$ between an aluminosilicate framework of stoichiometry $X\text{AlSi}_2\text{O}_6$ and a chloride-bearing hydrothermal fluid. These ion-exchange experiments were designed to provide direct thermodynamic data on the solid phases along the binary joins in the system KAlSi_2O_6 — $\text{RbAlSi}_2\text{O}_6$ — $\text{CsAlSi}_2\text{O}_6$ (Lagache 1974a) and inferred data for ternary compositions (Lagache 1974b). The same run products have now been studied by x -ray diffraction to illustrate the influence of compositional variation on cell edges and crystal symmetry. The study complements investigations of the effect of increasing temperature on cell edges and symmetry (Wyart 1938; Taylor & Henderson 1968; Peacor 1968; Bayer 1973).

Wyart (1938) found that KAlSi_2O_6 undergoes a displacive, non-quenchable structural transformation from a low-temperature tetragonal form to a high-temperature cubic polymorph; a increases and c decreases as leucite is heated. The cell edges converge to identical values as

the inversion temperature, 625°C , is approached. Peacor (1968) confirmed Wyart's findings but fixed the transformation temperature at $605 \pm 5^\circ\text{C}$ for leucites from Arricia and Vesuvius, Italy. The Vesuvius leucite was assumed to be $(\text{K}_{0.85}\text{Na}_{0.15})\text{AlSi}_2\text{O}_6$ for purposes of structure refinement at 635°C . Taylor & Henderson (1968) also documented the structural adjustments with heating experiments on all three end-members considered here. They proposed an inversion temperature of $605 \pm 5^\circ\text{C}$ for KAlSi_2O_6 and $310 \pm 5^\circ\text{C}$ for $\text{RbAlSi}_2\text{O}_6$; $\text{CsAlSi}_2\text{O}_6$ presumably transforms to a tetragonal form at a sub-zero temperature. The effect of increasing temperature apparently parallels that of replacing K or Rb by Cs, which also induces a structural transformation to cubic symmetry. However, the cell-edge and cell-volume data presented here are characterized by definite breaks, in contrast to the gradations found by Wyart (1938), Peacor (1968), and Taylor & Henderson (1968).

EXPERIMENTAL METHOD

The leucites and pollucites were synthesized at 600°C , 1 kbar, from gels of bulk composition $X\text{AlSi}_2\text{O}_6$, where $X = \text{K},\text{Rb}$, or Cs . In each experiment, the gel and 2M chloride solution of known composition exchanged alkalis. After the 10-day run, silicate and fluid were separated and analyzed by flame emission spectrophotometry, and in cases of trace quantities, by radioactive tracer technique using ^{86}Rb and ^{134}Cs . A precision of 5% is quoted for the analytical results (Lagache 1974a). Two additional runs were made at 1 kbar, 700°C to check the cell-dimension results of the 600°C synthesis of $\text{RbAlSi}_2\text{O}_6$. Run products were mixed with a small amount of a synthetic spinel as internal standard having $a = 8.0833\text{\AA}$ (G. V. Gibbs, pers. communication 1968) and x -rayed at room temperature with a Guinier-Hägg focusing powder camera ($\text{CuK}\alpha_1$ radiation, $\lambda = 1.54050\text{\AA}$).

The corrected 2θ values were uniquely indexed and used as input for the cell-parameter refinement program of Appleman & Evans (1973).

The run products nearest KAlSi_2O_6 in bulk composition typically consist of leucite with a minor sanidine impurity. The strongest lines of the impurity appear in the diffraction pattern, but not in sufficient number for determination of accurate cell dimensions. In what follows, the synthetic K-rich leucites are assumed to be on composition, *i.e.*, the impurity is assumed to contain alkalis in the same ratio as the bulk composition of solid reaction products. This assumption is justified by the small amount of impurity and by the direction of observed peak shifts in the impurity. None of the pollutants contains such impurities. However, an "impurity" problem also arises with the "first" one or two bulk compositions to yield a cubic phase in the series $\text{RbAlSi}_2\text{O}_6 - \text{CsAlSi}_2\text{O}_6$ and $\text{KAlSi}_2\text{O}_6 - \text{CsAlSi}_2\text{O}_6$. In these two-phase assemblages, the cubic phase clearly predominates, but one also finds the strong peaks of an accessory tetragonal phase. The two-phase assemblage may be stable or metastable, as will be evaluated in the discussion section. The cubic member of the two-phase assemblage is provisionally assigned the bulk composition of the solid reaction assemblage.

Join $\text{KAlSi}_2\text{O}_6 - \text{RbAlSi}_2\text{O}_6$

All fifteen bulk compositions along this join yield a tetragonal phase. Cell-parameter data are presented in Table 1, which incorporates the preliminary results of Martin & Lagache (1972). The progressive substitution of Rb for K leads to a marked increase in a and a slight, somewhat erratic decrease in c (Fig. 1). The cell volume also increases in linear fashion, the expected reflection of the substitution of a larger cation for a smaller one. Similar changes in a and c

are found when KAlSi_2O_6 is heated (Wyart 1938; Taylor & Henderson 1968).

Solution of calculated linear equations relating a , c , and V to mol fraction $\text{RbAlSi}_2\text{O}_6$ yield the following values for KAlSi_2O_6 : $a = 13.056$, $c = 13.762$, $V = 2344.7\text{\AA}^3$. It is convenient here to consider analogous equations covering tetragonal phases along the join $\text{KAlSi}_2\text{O}_6 - \text{CsAlSi}_2\text{O}_6$: KAlSi_2O_6 has $a = 13.056$, $c = 13.756$, $V = 2344.3\text{\AA}^3$. These calculated values compare well with Beswick's (1973) results for KAlSi_2O_6 synthesized at $T = 800^\circ\text{C}$, $P(\text{H}_2\text{O}) = 2000 \text{ kg/cm}^2$: $a = 13.057(3)$, $c = 13.752(5)$, $V = 2344.60(1.11)\text{\AA}^3$. The comparison is not as satisfactory with the results of Faust (1963), Henderson & Taylor (1969), and Suito *et al.* (1974). For a leucite synthesized at $T = 600^\circ\text{C}$, $P(\text{H}_2\text{O}) = 1 \text{ kbar}$, as in this study, Suito *et al.* (1974, Fig. 1) found $a = 13.05$, $c = 13.74$, $V = 2340\text{\AA}^3$. Here, c and V are slightly below our values. Henderson & Taylor (1969) report $a = 13.073(5)$, $c = 13.744(5)$, $V = 2348.9\text{\AA}^3$ for a leucite synthesized at 1100°C , $P = 1 \text{ atm}$. Faust (1963, Tables 4, 6) found $a = 13.074(3)$, $c = 13.738(3)$, $V = 2348.3\text{\AA}^3$ for a leucite synthesized at 1200°C , $P = 1 \text{ atm}$, from a mixture containing 0.10 wt % Na_2O and 0.04% CaO . These two leucites share a slightly lower c and higher a than the proposed values, leading to a somewhat larger unit-cell volume.

The results of Wyart (1938) and Barrer *et al.* (1953) depart from accepted values by such a wide margin that their validity must be questioned. Wyart (1938) used the oscillation technique to measure the cell dimensions of a single crystal synthesized at $T = 500^\circ\text{C}$ and low $P(\text{H}_2\text{O})$ from mixtures of silica, alumina and potash or muscovite, silica and potash (Friedel & Friedel 1890). The anomalous cell parameters, $a = 12.95$, $c = 13.65$, $V = 2289\text{\AA}^3$, may reflect departures from KAlSi_2O_6 bulk composition. The results reported by Barrer *et al.* (1953, Table 7) are similar: $a = 12.92$, $c = 13.70$, $V = 2287\text{\AA}^3$, perhaps for the same reason.

The calculated linear equations can also be solved for the cell parameters of pure $\text{RbAlSi}_2\text{O}_6$. From the join $\text{KAlSi}_2\text{O}_6 - \text{RbAlSi}_2\text{O}_6$, these are: $a = 13.299$, $c = 13.737$, $V = 2431.1\text{\AA}^3$. It is convenient to consider here equations covering tetragonal phases along the join $\text{RbAlSi}_2\text{O}_6 - \text{CsAlSi}_2\text{O}_6$: these give $a = 13.296$, $c = 13.751$, $V = 2430.7\text{\AA}^3$ for $\text{RbAlSi}_2\text{O}_6$. The discrepancy in the two estimates stems from an anomaly in the product of the 1 kbar, 600°C synthesis of $\text{RbAlSi}_2\text{O}_6$ (Table 1). Its c is reproducibly 0.01\AA greater than expected. Products of two syntheses at 700°C give values of c more in line with

TABLE 1. CELL PARAMETERS OF $(\text{K}_{1-x}\text{Rb}_x)\text{AlSi}_2\text{O}_6$ SYNTHESIZED AT 600°C , 1 KBAR, AND QUENCHED TO ROOM TEMPERATURE.

100x	a(Å)	a(Å)	V(Å ³)	standard error (°2σ)
0	13.0499(6)	13.7532(10)	2342.16(.22)	0.009
0	13.0584(10)	13.7802(19)	2346.42(.38)	0.012
0.49	13.0562(8)	13.7591(11)	2345.45(.28)	0.008
2.48	13.0590(9)	13.7577(16)	2346.19(.31)	0.009
5.62	13.0735(11)	13.7615(24)	2352.07(.43)	0.013
8.5	13.0755(5)	13.7554(8)	2351.77(.18)	0.009
9.15	13.0782(7)	13.7563(12)	2352.86(.25)	0.008
17	13.0991(5)	13.7520(9)	2359.64(.19)	0.009
26	13.1192(7)	13.7520(11)	2366.91(.25)	0.011
35.5	13.1420(4)	13.7450(7)	2373.92(.17)	0.008
45	13.1699(9)	13.7435(13)	2383.77(.30)	0.012
55.5	13.1947(10)	13.7463(16)	2393.22(.38)	0.016
66	13.2182(8)	13.7461(10)	2401.73(.28)	0.011
77	13.2442(10)	13.7444(18)	2410.89(.39)	0.016
88	13.2687(8)	13.7445(16)	2419.85(.31)	0.013
100	13.2972(10)	13.7572(20)	2432.50(.38)	0.015
100*	13.2967(25)	13.7495(34)	2430.79(.92)	0.023
100+	13.2975(22)	13.7451(40)	2430.46(.82)	0.022

* $\text{RbAlSi}_2\text{O}_6$ gel + H_2O , $T = 700^\circ\text{C}$, $P(\text{H}_2\text{O}) = 1 \text{ kbar}$

+ $\text{RbAlSi}_2\text{O}_6$ gel + H_2O + RbCl , $T = 700^\circ\text{C}$, $P(\text{H}_2\text{O}) = 1 \text{ kbar}$

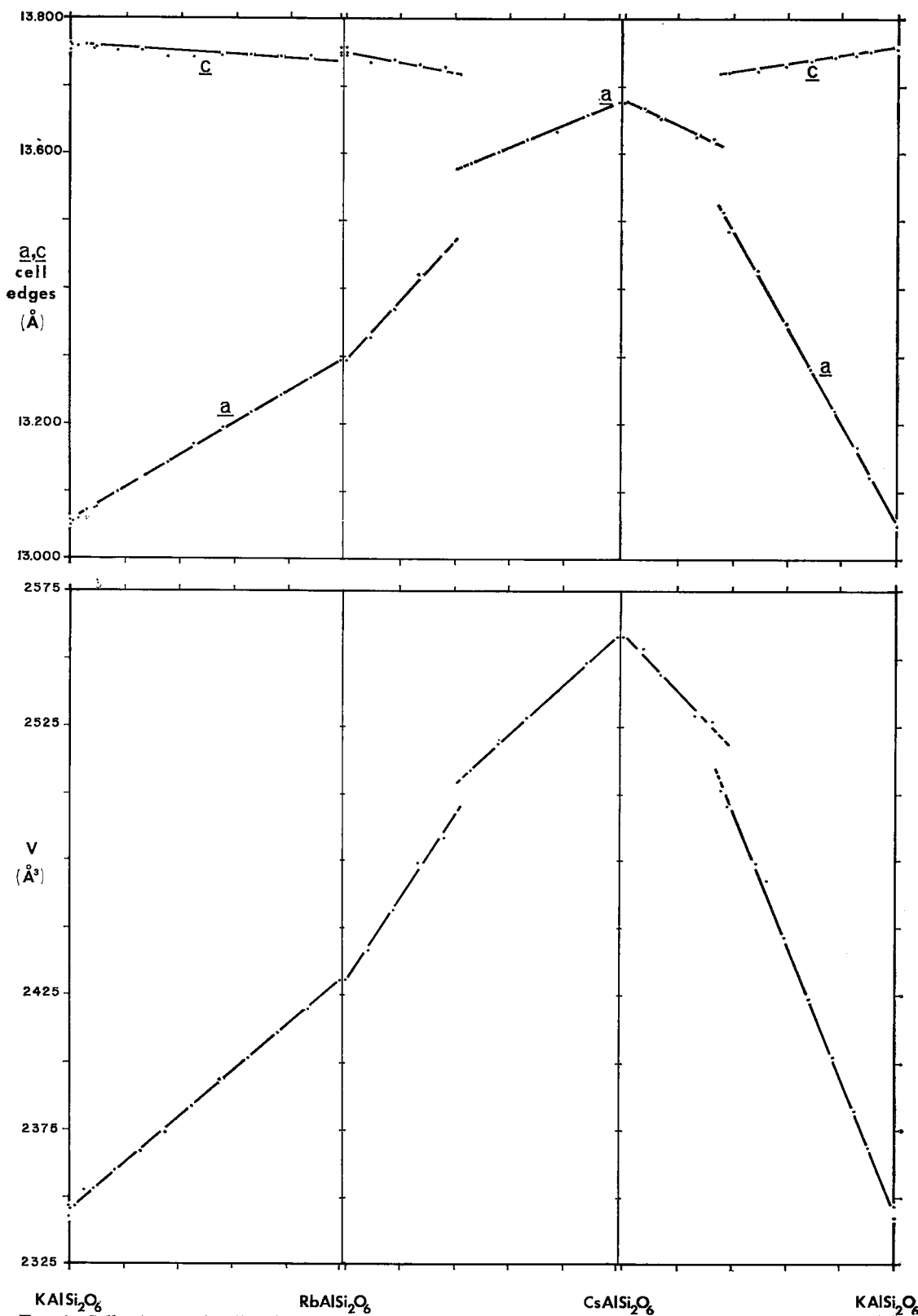


FIG. 1. Cell edges and cell volume of synthetic leucites and pollucites in the system KAlSi_2O_6 - $\text{RbAlSi}_2\text{O}_6$ - $\text{CsAlSi}_2\text{O}_6$ - KAlSi_2O_6 .

expected values (Tables 1, 2). This unexplained aberration is minor, however, compared to the range of values to be found for $\text{RbAlSi}_2\text{O}_6$ in the literature. Henderson & Taylor (1969) find $a = 13.334(5)$, $c = 13.672(5)$, $V = 2430.8\text{\AA}^3$ for $\text{RbAlSi}_2\text{O}_6$ synthesized at 1100°C , $P = 1$ atm. They also report less precise data for two Rb-leucites synthesized hydrothermally from $\text{RbAlSi}_2\text{O}_6$ gel at a temperature between 650 and 750°C and $P(\text{H}_2\text{O}) = 1$ kbar: $a = 13.30$, $c = 13.73$, $V = 2428.7\text{\AA}^3$, and $a = 13.30$, $c = 13.67$, $V = 2429.0\text{\AA}^3$. As was the case with KAlSi_2O_6 , their cell volumes agree with our proposed value, but their a is consistently higher and, in two cases, their c is unusually low. Beswick (1973) reports $a = 13.282(8)$, $c = 13.708(11)$, $V = 2418.15(2.59)\text{\AA}^3$ for Rb-leucite synthesized from a $\text{RbAlSi}_2\text{O}_6$ gel at $T = 800^\circ\text{C}$, $P(\text{H}_2\text{O}) = 2000$ kg/cm². Here, both a and c fall below expected values. Finally, Barrer & McCallum (1953) and Barrer *et al.* (1953) provide data for two "polymorphic forms of Rb-analcite": Rb-analcite I (PDF 10-384) has $a = 13.2$, $c = 13.6$, $V = 2370\text{\AA}^3$; Rb-analcite II (PDF 10-385) has $a = 13.64$, $c = 13.33$, $V = 2480\text{\AA}^3$. Neither set of results agrees with the observed range of values, Rb-analcite I having a smaller cell volume, Rb-analcite II a larger one. No evidence has been found in this study for two polymorphic forms of tetragonal $\text{RbAlSi}_2\text{O}_6$. Again, the possibility of departures from stoi-

chiometry must be entertained, especially in view of the qualification that "Rb-analcite II" is a run product only where the gel starting material is enriched in silica with respect to $\text{RbAlSi}_2\text{O}_6$. It was found in 200°C runs with starting materials of general formula $\text{Rb}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2$ where n ranged from 6 to 10 (Barrer & McCallum 1953, Table 2). Henderson & Taylor (1969) also report the synthesis of a tetragonal phase from a starting material of bulk composition $\text{RbAlSi}_2\text{O}_6$ at 1230°C , $P(\text{H}_2\text{O}) = 1$ kbar, but do not give cell dimensions.

Join $\text{RbAlSi}_2\text{O}_6$ — $\text{CsAlSi}_2\text{O}_6$

Cell-dimension data are provided in Table 2 for eleven bulk compositions along the join $\text{RbAlSi}_2\text{O}_6$ — $\text{CsAlSi}_2\text{O}_6$. The break in the series between tetragonal and cubic products occurs between 36.0 and 45.8 mol % $\text{CsAlSi}_2\text{O}_6$ (Fig. 1), subject to the uncertainty discussed earlier. As reported by Černý (1974, Fig. 8), the progressive addition of cesium, a highly absorbing atom for $\text{CuK}\alpha_1$ radiation, is reflected by marked reductions in many diffraction intensities, as well as by the expected peak shifts.

Join KAlSi_2O_6 — $\text{CsAlSi}_2\text{O}_6$

Cell-dimension data are presented in Table 3 and Figure 1 for fourteen bulk compositions along this join. As with the join $\text{RbAlSi}_2\text{O}_6$ — $\text{CsAlSi}_2\text{O}_6$, and in roughly the same cell-volume interval, a first-order break is encountered between tetragonal and cubic phases, in the composition interval 64.0 to 67.5 mol % $\text{CsAlSi}_2\text{O}_6$. These findings disagree in part with the preliminary data presented for the join by Suito *et al.* (1974, Fig. 1). Their data on eight bulk compositions also crystallized at $T = 600^\circ\text{C}$, $P(\text{H}_2\text{O}) = 1$ kbar suggest a discontinuity near the 65 mol % $\text{CsAlSi}_2\text{O}_6$ composition, in agreement with our findings. However, their Figure 1 shows a gradual convergence of a and c cell edges to a unique value, as if the phase transformation were second- or higher-order, rather than first-order as documented in this study. Their interpretation relies heavily on the cell edges they report for the 65 mol % $\text{CsAlSi}_2\text{O}_6$ bulk composition.

Solution of the linear equations describing a and V as a function of composition for 100% $\text{CsAlSi}_2\text{O}_6$ gives: $a = 13.677\text{\AA}$, $V = 2558.3\text{\AA}^3$ from the series $\text{RbAlSi}_2\text{O}_6$ — $\text{CsAlSi}_2\text{O}_6$, $a = 13.680\text{\AA}$, $V = 2559.9\text{\AA}^3$ from the series KAlSi_2O_6 — $\text{CsAlSi}_2\text{O}_6$. These results fall in the

TABLE 2. CELL PARAMETERS OF $(\text{Rb}_{1-y}\text{Cs}_y)\text{AlSi}_2\text{O}_6$ SYNTHESIZED AT 600°C , 1 KBAR, AND QUENCHED TO ROOM TEMPERATURE.

100y	a(Å)	c(Å)	V(Å ³)	standard error (°2σ)
8.6	13.3307(12)	13.7376(17)	2441.27(.44)	0.013
17.5	13.3718(14)	13.7401(19)	2456.78(.49)	0.011
26.5	13.4222(25)	13.7337(34)	2474.18(.86)	0.023
36.0	13.4503(24)	13.7292(37)	2483.74(.81)	0.020
45.8*	13.5880(16)		2508.79(.86)	0.021
55.8*	13.6050(15)		2518.23(.82)	0.014
66.4	13.6229(11)		2528.19(.64)	0.015
77.2	13.6345(12)		2534.65(.66)	0.018
88.4	13.6593(11)		2548.52(.62)	0.017
100	13.6773(14)		2558.61(.80)	0.020

*Two-phase assemblage containing a small amount of the tetragonal phase.

TABLE 3. CELL PARAMETERS OF $(\text{K}_{1-x}\text{Cs}_x)\text{AlSi}_2\text{O}_6$ SYNTHESIZED AT 600°C , 1 KBAR, AND QUENCHED TO ROOM TEMPERATURE.

100x	a(Å)	c(Å)	V(Å ³)	standard error (°2σ)
9.8	13.1238(7)	13.7511(12)	2368.43(.27)	0.012
15.0	13.1645(12)	13.7454(16)	2382.13(.43)	0.018
23.0	13.2213(7)	13.7418(9)	2402.11(.26)	0.009
31.8	13.2828(15)	13.7371(20)	2423.68(.51)	0.017
41.0	13.3492(8)	13.7305(13)	2446.78(.30)	0.012
51.3	13.4275(8)	13.7234(13)	2474.30(.31)	0.010
62.0	13.4875(14)	13.7192(15)	2495.68(.47)	0.010
64.0	13.5137(30)		2506.74(1.02)	0.020
67.5*	13.6214(24)		2527.34(1.36)	0.025
73.7	13.6255(17)		2529.62(.95)	0.019
86.3	13.6527(20)		2544.81(1.13)	0.024
92.7	13.6694(14)		2554.16(.79)	0.018

*Two-phase assemblage containing a small amount of the tetragonal phase.

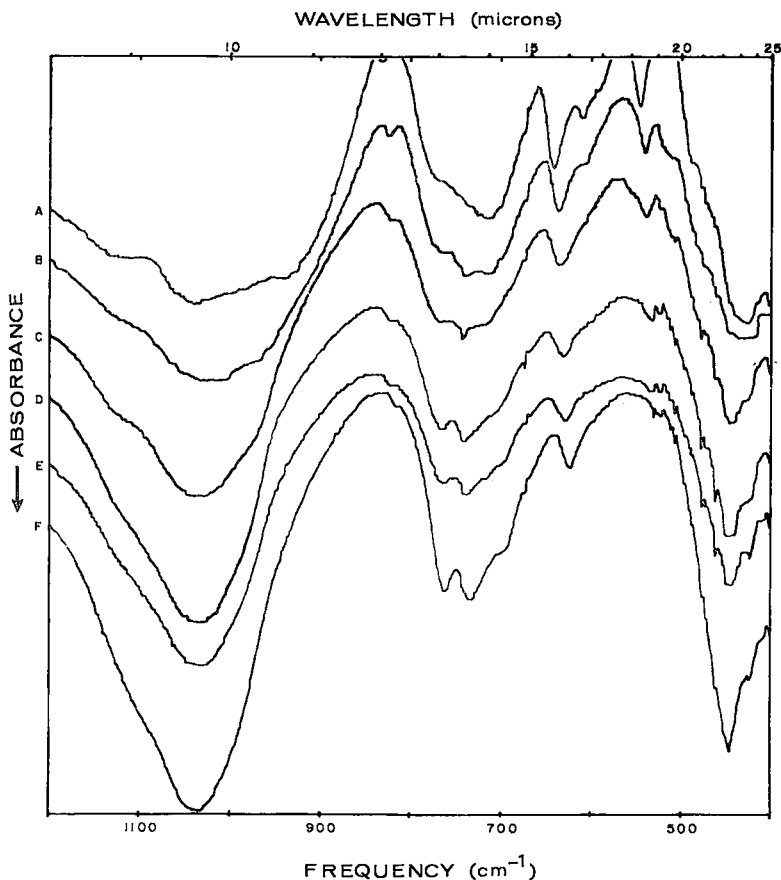


FIG. 2. Infrared absorption spectra of selected synthetic leucites and pollucites in the system $\text{KAlSi}_2\text{O}_6\text{-RbAlSi}_2\text{O}_6\text{-CsAlSi}_2\text{O}_6$.

upper part of the range of values reported for synthetic pollucites. Kume & Koizumi (1965) report $a = 13.653\text{\AA}$ for $\text{CsAlSi}_2\text{O}_6$ synthesized at $T = 450^\circ\text{C}$, $P(\text{H}_2\text{O}) = 1000\text{ kg/cm}^2$. Barrer *et al.* (1953, Table 7) synthesized pollucite having $a = 13.66\text{\AA}$ in the interval $160\text{-}450^\circ\text{C}$ and at low water pressure. Suito *et al.* (1974, Fig. 1) synthesized $\text{CsAlSi}_2\text{O}_6$ with $a = 13.685\text{\AA}$, $T = 600^\circ\text{C}$, $P(\text{H}_2\text{O}) = 1\text{ kbar}$, and Henderson & Taylor (1969) found $a = 13.682\text{\AA}$ in their 1100°C , 1 atm. run-product.

INFRARED ABSORPTION DATA

Infrared absorption spectra were obtained for the synthetic leucites and pollucites to confirm the anhydrous nature of the product, by the absence of absorptions in the $3000\text{-}3500\text{ cm}^{-1}$ region, and to provide additional signs of the structural changes. All spectra were obtained on a Perkin-Elmer model 337 grating infrared spectrophotometer, using KBr pellets with 0.20

weight % sample concentration (Lyons 1966). Polystyrene absorptions serve to standardize the spectra. Portions of six spectra are reproduced (Fig. 2). Spectra A, C, and F belong to the end-member compositions KAlSi_2O_6 , $\text{RbAlSi}_2\text{O}_6$, and $\text{CsAlSi}_2\text{O}_6$. Spectrum B represents an intermediate K-Rb leucite, and spectra D and E belong to compositions that straddle the first-order break in the series $\text{RbAlSi}_2\text{O}_6\text{—CsAlSi}_2\text{O}_6$. The sequence of presentation of spectra in Figure 2 reflects the increasing mean radius of the monovalent cation.

A number of changes can be correlated with the increase in mean atomic radius of the alkali. One of these occurs in the $900\text{-}1100\text{ cm}^{-1}$ region of the spectrum. Leucite has two major absorptions at approximately 940 and 1040 cm^{-1} . In Rb-leucite, the 1040 cm^{-1} absorption predominates, with a suggestion of a subsidiary absorption at 975 cm^{-1} . A single major absorption occurs at 1035 cm^{-1} in pollucite; it is more in-

tense than in spectra D and E. Another distinct absorption in leucite is found at approximately 830 cm^{-1} . This one shifts progressively to lower frequencies and lower intensity and poorer resolution in the sequence A to F until it is barely discernible near 815 cm^{-1} in spectrum F. Other absorptions behave similarly in the interval 500 to 650 cm^{-1} . In contrast, the regions between 700 and 800 cm^{-1} and between 400 and 500 cm^{-1} demonstrate a reverse trend, with absorptions shifting to higher frequencies and increasing in resolution and intensity in the sequence A to F.

Although the absorptions are not correlated with specific interatomic bonds, the progressive nature of the changes is consistent with a steady progression towards a fully-expanded cubic structure at room temperature. The progression continues even once a cubic structure has been attained (*cf.* spectra E and F, Fig. 2). The change from a tetragonal structure in which $a = 13.4503$, $c = 13.7292\text{ \AA}$ (spectrum D) to a cubic structure in which $a = 13.5880\text{ \AA}$ (spectrum E) does not result in significant changes in appearance of the infrared absorption spectrum.

DISCUSSION

By measuring partition coefficients between silicate and fluid along all three binary joins in the system $\text{KAlSi}_2\text{O}_6 - \text{RbAlSi}_2\text{O}_6 - \text{CsAlSi}_2\text{O}_6$, Lagache (1974a) showed that at 600°C , 1 kbar, the larger monovalent cation is consistently enriched in the cubic aluminosilicate structure. The coexisting chloride-bearing hydrothermal fluid is correspondingly depleted in the same cation. These findings suggest that at 600°C , and thus also at room temperature, potassium cannot fill the available site completely. In fact, Wyart (1940, p. 12) found that at room temperature, the tetragonal structure contains potassium atoms surrounded by twelve oxygen atoms at a relatively large mean distance of 3.5 \AA . Peacor (1968) confirmed these bond lengths in a refinement of the cubic structure of $\text{K}_{0.88}\text{Na}_{0.15}\text{AlSi}_2\text{O}_6$ at 635°C . Cesium most nearly fills the cavity at 600°C , and must fill it even more so at lower temperatures, as reflected in the persistence of the cubic form of pollucite to room temperature. In contrast, the rubidium and potassium compounds undergo a displacive transformation in which the $(\text{Si,Al})\text{O}_4$ tetrahedra undergo slight rotations that lead to loss of symmetry. The rapidity of the response to thermal treatment precludes the possibility of an Al-Si order-disorder relationship between high- and low-temperature forms (Peacor 1968, p. 219).

The effects of heating these structures and of substituting a larger cation for a smaller one are found to be very similar; in both cases, a and V increase, and c contracts slightly. The infrared absorption data obtained at room temperature suggest that the structural changes incurred as cesium is progressively added are completely gradational, and continue even after a cubic structure has been stabilized. Similarly, the heating experiments of Taylor & Henderson (1968) demonstrate gradual changes in all three end-members. They document an initial rapid increase in cell volume of leucite and Rb-leucite up to the inversion temperature, reflecting the expansion and rotation of $(\text{Si,Al})\text{O}_4$ tetrahedral units. Beyond the transition temperature, they distinguish an interval in which thermal expansion continues at a lower rate, followed by a higher-temperature interval where changes in the cubic structure occur at a much reduced rate, presumably because the tectosilicate framework is fully expanded.

Two hypotheses may be advanced, depending on the interpretation proposed for the two-phase assemblages. Heating leucite and Rb-leucite leads to a displacive, non-quenchable, and therefore second- or higher-order transformation devoid of hysteresis effects (Wyart 1938; Peacor 1968; Taylor & Henderson 1968). For the case of decreasing temperature from 600°C , a plot of unit-cell volumes of leucite and Rb-leucite at the inversion versus inversion temperature (Henderson & Taylor 1969) suggests that a cubic phase having V approximately 2520 \AA^3 will transform to a tetragonal structure near room temperature. This predicted volume agrees very well with observed volumes of the cubic phases at the break found along the joins $\text{KAlSi}_2\text{O}_6 - \text{CsAlSi}_2\text{O}_6$ and $\text{RbAlSi}_2\text{O}_6 - \text{CsAlSi}_2\text{O}_6$. Thus for purely kinetic reasons, two phases, one stable, the other metastable, could coexist for those bulk compositions having inversions near room temperature. However, another possibility, consistent with the cell-dimension data and perhaps also with the complications in the inversion noted by Faust (1963) in differential thermal analysis patterns, would provide two stably co-existing solids of slightly different compositions at a given temperature, generating a two-phase loop or volume in $T-X$ sections of appropriate binary or ternary systems. Favouring this proposal are 1) the probability that stably-coexisting tetragonal and cubic structures will not accept cesium to the same extent, which can best be evaluated by cell-dimension determinations of coexisting phases in fine-grained aggregates, and 2) the analogies that can be made with the system nepheline-

kalsilite, where two structurally and compositionally distinct nephelines may coexist isothermally. The same behaviour may also characterize the monoclinic-triclinic "displacive" transformation in the feldspar system. Implicit in this hypothesis is that only KAlSi_2O_6 and $\text{RbAlSi}_2\text{O}_6$ would show true polymorphism.

These complications rule out, for temperatures below 600°C , the continuous solid-solution series based on the alkali-exchange data obtained at 600°C by Lagache (1974a, b). The departures from ideal solid solutions noted at 600°C along the three binary joins will increase with decreasing temperature, and will lead to the stabilization of the tetragonal structure. Studies employing high-temperature diffraction techniques coupled with differential thermal analysis of individual compositions will be needed to verify the proposals made here, 1) that the displacive transformation attributed to leucite may be restricted to KAlSi_2O_6 and $\text{RbAlSi}_2\text{O}_6$, and 2) that the first-order break observed in compositional transitions upon replacement of K or Rb by Cs serves as a model for the behaviour of binary and ternary leucites in the system $\text{KAlSi}_2\text{O}_6 - \text{RbAlSi}_2\text{O}_6 - \text{CsAlSi}_2\text{O}_6$ as they invert to the cubic structure upon heating.

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