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Interstitial Cristobalite-type Compounds $(Na_2O)_{\leq 0.33}Na[AlSiO_4]$

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The series of interstitial compounds $(Na_2O)_{\leq 0.33}Na[AlSiO_4]$ exhibits the cubic symmetry of the cristobalite type $Na[AlSiO_4]$-carnegieite host lattice as concentrations of 0.01–0.33 Na_2O are intercalated at elevated temperatures under closed system conditions (950–1100 K). The tetrahedral framework structure of the host lattice expands correspondingly from $a = 7.3001(5)$ to 7.3029(1) Å. The structure model of the end member, $(Na_2O)_{0.33}Na[AlSiO_4)$, proposed from structure factor calculations based on X-ray powder diffraction data, shows unique (Na,O)–(Na,O) distances in the high-temperature form of 3.17 Å. A total of 6⅔ sodium atoms and 1⅓ oxygens statistically occupying the cage like 12-fold oxygen-coordinated position of space group $F\bar{4}3m$ form a diamond-type sublattice in the high-cristobalite-type "host lattice" $[AlSiO_4]^{1-}_{3d\infty}$. Superstructure characteristics on X-ray Guinier powder diffraction data indicate complex ordering mechanisms following long-term annealing (200 hr, 370–970 K). At temperatures >1350 K in an open system, intercalated Na_2O is released with the subsequent collapse of the $Na[AlSiO_4]$ host lattice from cubic to triclinic, the regular symmetry of $Na[AlSiO_4]$-carnegieite at temperatures <960 K. © 1986 Academic Press, Inc.

Introduction

Carnegieite is the well-known high-temperature form of $Na[AlSiO_4]$-nepheline, which can easily be prepared by annealing nepheline beyond 1530 K with subsequent quenching to room temperature. The cristobalite-like structure of carnegieite exhibits cubic symmetry at elevated temperatures (*1*). Upon cooling, to 968 K, however, a reversible first-order phase transition takes place yielding a carnegieite-like phase of lower symmetry (Fig. 1). Triclinic symmetry has been proven for this cristobalite-like low-temperature form of $Na[AlSiO_4]$ by means of combined electron (TEM) and high-resolution X-ray diffraction work (*2*). Following some preliminary studies on carnegieitelike-stuffed derivatives of cristobalite (*3, 4, 11*) we report here successful intercalation of sodium oxide into $Na[AlSiO_4]$-type nepheline-carnegieite. Special attention has been paid to the verification of pure phase samples by high-resolution powder diffraction and thermoanalytical data. In a forthcoming paper, which directly refers to the recently given transport properties of materials of the substitution series $Na_{1+x}Al_{1+x}Si_{1-x}O_4$ with $x \leq 0.7(4)$ or compounds $Na[AlSiO_4] \cdot xNa_2O$ with $x = 0.25$, $x = 0.5(11)$, we will discuss the data on ionic conductivity of our Na_2O-stuffed derivatives of cristobalite $(Na_2O)_{\leq 0.33}Na[AlSiO_4)$.[1]

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[1] We prefer the term interstitial compounds for this series because the intercalated Na_2O might be thermally evaporized at elevated temperatures ($T >$ 1350

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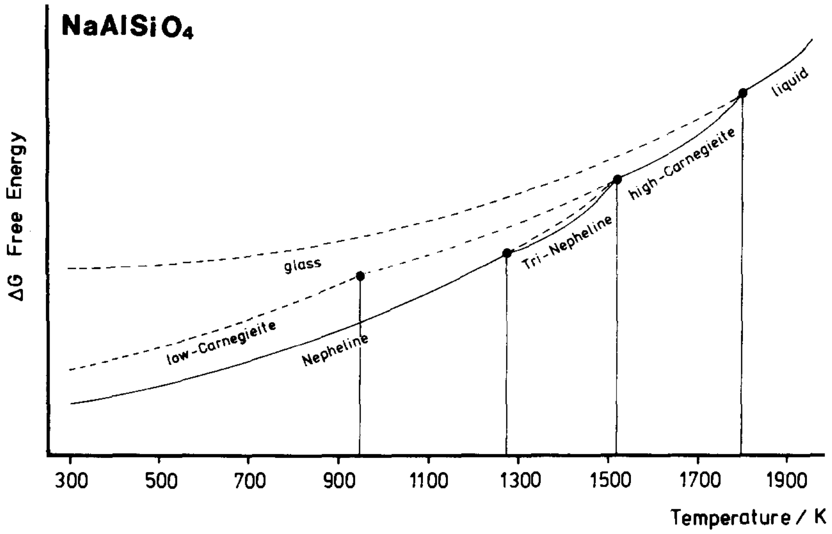

FIG. 1. Temperature-induced phase transitions of SiO_2-stuffed derivatives of composition Na[Al SiO_4]. All but one phase transition show a strong time dependency. The only fully reversible phase transition has been observed for the high- ⇌ low-carnegieite transition at 968 K (*3*, *7*). Long-term annealing at temperatures 1250–1525 K starting either from hexagonal nepheline or cubic high-carnegieite yields the trinepheline phase (a = 8.659(2), b = 14.942(3), c = 25.106(5) Å), known so far only from hydrothermal synthesis (*9*). Recrystallization and phase formation from supercooled Na[$AlSiO_4$] melts at temperature <1790 K is strongly controlled by kinetics and the thermal history of the (supercooled) melts (*10*).

Experimental

Starting either from Na[$AlSiO_4$]-nepheline or corresponding oxides Al_2O_3 (Merck 1095), SiO_2 (Aerosil, Degussa) and Na_2O, which had been obtained by calcinating Na_2CO_3 (Merck 6392), various mixtures of composition Na_2O : Na[$AlSiO_4$] = 0.1 : 1 to 2 : 1 were prepared at elevated temperatures (770–1870 K) under different experimental conditions (Fig. 2). Pellets of fine grained materials (0.1 to 10-μm grain size), pressed at hydrostatic pressures of 1000 kg/cm^2 were annealed under a nitrogen atmosphere (N_2, 99.999%, normal pressure, flow rate 2.0 l/hr) in closed platinum crucibles, in several cycles of reactivation.

During preliminary experiments this open system type of reaction has been examined by thermogravimetry (Netzsch Thermoanalyzer STA-429/Balzers QMG-511-mass spectrometer) and X-ray powder diffraction (Guinier–Huber System 600, CuK_{α_1}-radiation) in order to quantify the Na_2O effusion rates at temperatures >1370 K and the corresponding formation of solid phases. Loss of Na_2O has been compensated until equilibrium of crystalline phases had been reached after several cycles of annealing, grinding, and subsequent pressing of pellets under identical experimental conditions. In order to avoid any gradient in the Na_2O concentration within a sample due to evaporization during the period of reaction, graphite miniautoclaves with

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K) without destroying the cristobalite-like framework structure of carnegieite. Evaporization of Na_2O from charge-coupled (Na^+ + Al^{3+} → Si^{4+}) "stuffed derivatives of SiO_2" (M. Buerger, 1947) has not been observed below the melting point of carnegieite Na[Al SiO_4] (Figs. 1, 2).

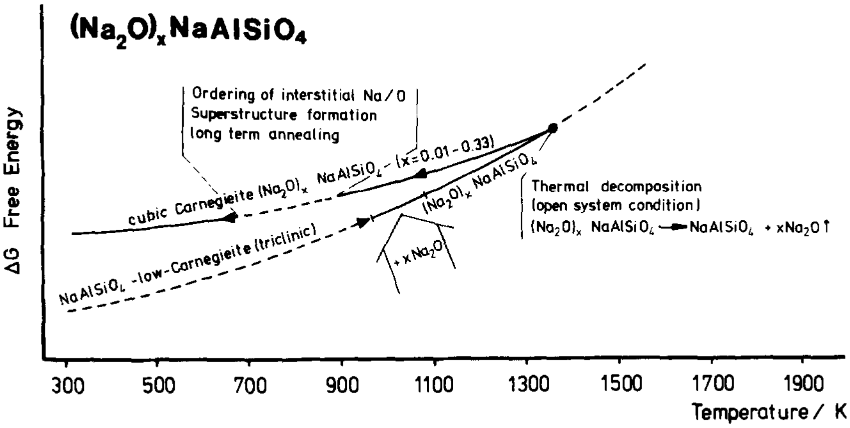


FIG. 2. Temperature-induced phase relations of interstitial compounds $(Na_2O)_xNa[AlSiO_4]$, $0.01 < x < 0.33$. Na_2O is intercalated into carnegieite—serving as the host lattice—at elevated temperatures 950–1100 K. Intercalation was found to be unsuccessful with nepheline serving as the host lattice. Interstitial Na_2O stabilizes the cubic form of carnegieite down to room temperature. At temperatures >1375 K interstitial Na_2O is released from the host lattice at open system conditions. A collapse of the tetrahedral network of carnegieite from cubic to triclinic symmetry occurs at temperatures <968 K upon cooling.

thread fastening (graphite 99.999%, Schunk & Ebe) were used. The autoclaves (ϕ: 6 mm, h: 30 mm) were completely filled with highly compressed samples. Unfortunately, this type of container was not successful for longer reaction periods. At $t > 1$ hr considerable loss of Na_2O was observed at annealing temperatures of 1370–1870 K.

Additional experiments in closed systems have been carried out in order to obtain single crystals of the interstitial compounds. Cylindrical vessels of platinum (ϕ: 6 mm, h: 50 mm) sealed with an H_2/O_2 flame and electro-welded (He, Ar protection gas) tantalum containers have been employed for crystal growth experiments at temperatures 1370–1770 K. Temperature gradients of 10–50 K from top to bottom of the closed reaction vessels have been applied in order to favor the formation of single crystals by chemical transport by Na_2O which had been provided in excess in various proportions. No loss of Na_2O due to the considerable Na_2O-partial pressure at elevated temperatures during this type of

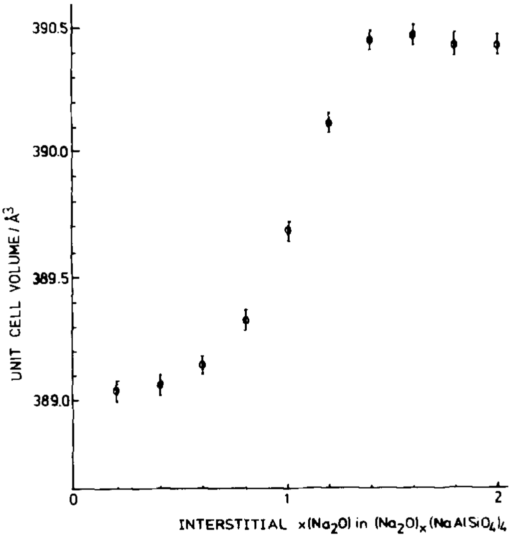


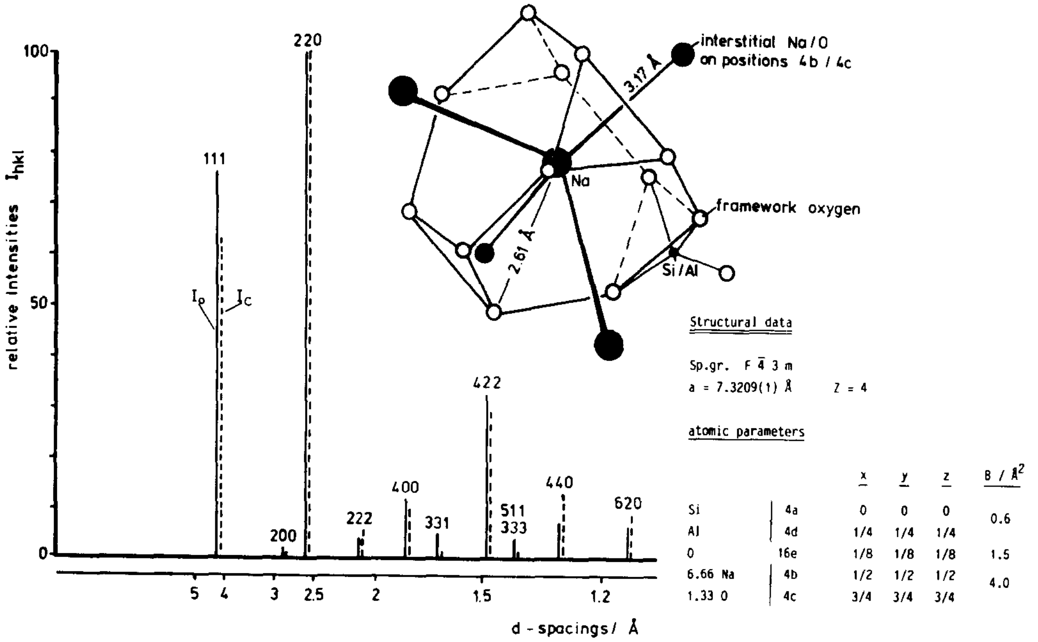
FIG. 3. Increase of unit cell volume of cubic $Na[AlSiO_4]$-carnegieite (host lattice) as the concentration of interstitial Na_2O is increased from 0.00 to 2.00 formula units per cell in intercalation experiments in closed systems, 950–1100 K. The structure expands to the maximum when 1.33 Na_2O/unit cell is introduced to the interstitial space.

closed system reaction was observed weighting.

In order to avoid the swelling of the platinum capsules at elevated temperatures and subsequent tearing of the metal, a special counterpressure technique has been applied. The wall of the reaction vessel has been stabilized through embedding the platinum capsules into a matrix of 1-μm-grain corundum and subsequent squeezing of the assemblage by outer pressures up to 100 kg/cm^2. Reaction experiments up to temperatures of 1770 K have been carried out successfully without considerable loss in Na_2O this way. Hydrothermal synthesis have been carried out at pressures 500–700 bar and temperatures 670–820 K with various sample compositions sealed in silver capsules.

Finally, different flux methods have been applied, selecting $NaNO_3$, NaCl, NaF, Na_2SO_4, and $Na_2B_4O_7$ as mineralizes for single crystal growth at temperatures 870–1470 K, in order to increase our chances to obtain single crystals, or at least fractions of larger grain sizes (>10 μm) of the novel cristobalite-type intercalation compounds.

The chemical constitution of samples after intercalation of Na_2O or from annealing experiments has been determined by combined analyses. The crystalline phases have been identified by high-resolution Guiner X-ray powder diffraction techniques up to 1270 K and by optical polarization microscopy employing heating stages up to 1670 K. Data on chemical composition have been supplied by microprobe (Cameca, Camebax–Micro) and X-ray fluorescence analysis (Kevex 0700-system). The content of Na_2O has been checked by AAS and complexometric titration. Thermogravimetry and mass spectrometry (Mettler ther-



Structural data

Sp.gr. $F\bar{4}3m$
a = 7.3209(1) Å Z = 4

atomic parameters

		x	y	z	B / Å^2
Si	4a	0	0	0	0.6
Al	4d	1/4	1/4	1/4	
O	16e	1/8	1/8	1/8	1.5
6.66 Na	4b	1/2	1/2	1/2	4.0
1.33 O	4c	3/4	3/4	3/4	

FIG. 4. Structure model of interstitial cristobalite-like phases $(Na_2O)_xNa[AlSiO_4]$. I_0 data of the $x = 0.33$ reference phase from Guinier-powder diffraction ($2\theta < 80°$) meets the given I_0 data with $R = 0.11$. Statistical occupation of 6.66 sodium and 1.33 oxygen in positions 4*b*/4*c* of space group $F\bar{4}3m$ reveals the conflict of short interstitial–framework O distances = 2.61 Å and (Na,O)–(Na,O) = 3.17 in the quenched sample, prepared at elevated temperatures 950–1100 K.

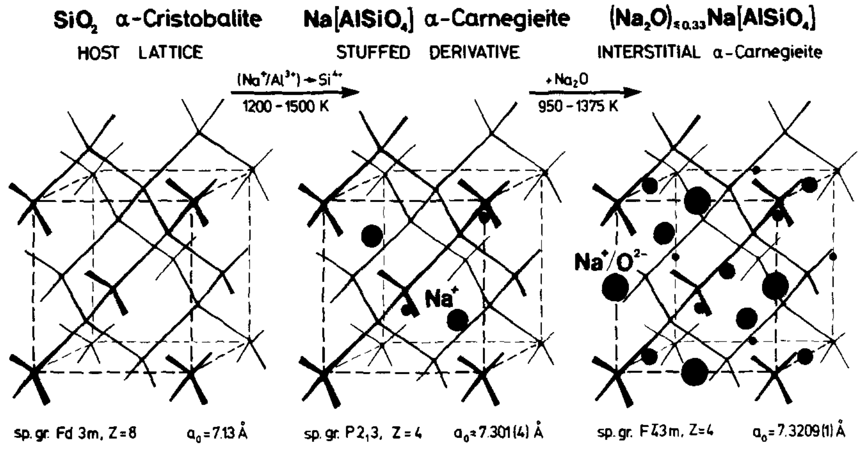


FIG. 5. Three-dimensional diamond-like network of $[Si,AlO_{4/2}]^-$-tetrahedra (*8*). Four Na^+ cations inserted in high-carnegieite $Na[AlSiO_4]$ (mid) (*6*) or additional Na_2O inserted in interstitial compounds $(Na_2O)_{\leq 0.33}[NaAlSiO_4]$, assuming statistical distribution of all Na^+ cations and oxygens on positions 4*b*/4*c* in space $F\bar{4}3m$ (Na : O = 5 : 1), confirm that all nonframework constituents in this model (right) form a diamond-like sublattice within the cristobalite-like $[SiAlO_4]^-$ skeleton.

moanalyzer TA1; Netzsch STA 429; Balzers QMG-511) have been employed to identify any interaction of the alkali-rich samples with water or CO_2 from the atmosphere at arbitrary temperatures up to 1870 K. Because of the highly hygroscopic character of compositions $(Na_2O)_nNa[AlSiO_4]$, $n > 0$, samples were transported to the analysis

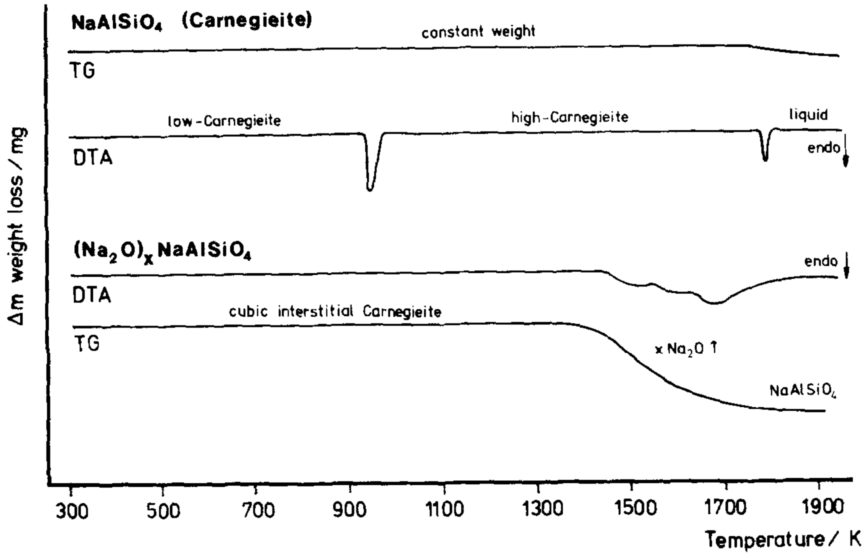


FIG. 6. Thermoanalytical control of release of Na_2O from interstitial $(Na_2O)_{0.33}Na[AlSiO_4]$-carnegieite as compared to the thermal decomposition characteristics of the blank host compound, $Na[AlSiO_4]$-carnegieite. Thermogravimetric "TG" and "DTA" data of samples equal to weight from run 5 K/min 99.999% N_2 atmosphere.

equipment under a N_2 atmosphere (99.999%). Structure factor calculations have been carried out employing the program LAZY PULVERIX (5).

Results and Discussion

Synthesis of a series of compositions $n\mathrm{Na_2O} + \mathrm{Na[AlSiO_4]}$ ($0 < n < 2$) showed a distinct limit for substitution when $\mathrm{Na_2O} > 0.33$. From X-ray powder diffraction Guinier film data a significant increase in the unit cell volume with increasing $\mathrm{Na_2O}$ content was found for $n = 0.01$ to 0.33 (Fig. 3). Amounts of $\mathrm{Na_2O}$ smaller than 0.01 $\mathrm{Na_2O}$ failed to stabilize the cubic symmetry of high-carnegieite $\mathrm{Na[AlSiO_4]}$ at temperatures <960 K, upon quenching the annealing products from temperatures 1070–1670 K to room temperature. The triclinic phase of low carnegieite has unambiguously been identified for $\mathrm{(Na_2O)_{\leq 0.01}Na[AlSiO_4]}$ (*2*). The powder diffraction data of cubic $\mathrm{(Na_2O)_{0.33}Na[AlSiO_4]}$ is given in Table I together with that of the host structure. Structure factor calculations on $\mathrm{(Na_2O)_{0.33}Na[AlSiO_4]}$ (Fig. 4), assuming a statistical distribution of $6\frac{2}{3}$ $\mathrm{Na^{1+}}$ and $1\frac{1}{3}$ $\mathrm{O^{2-}}$

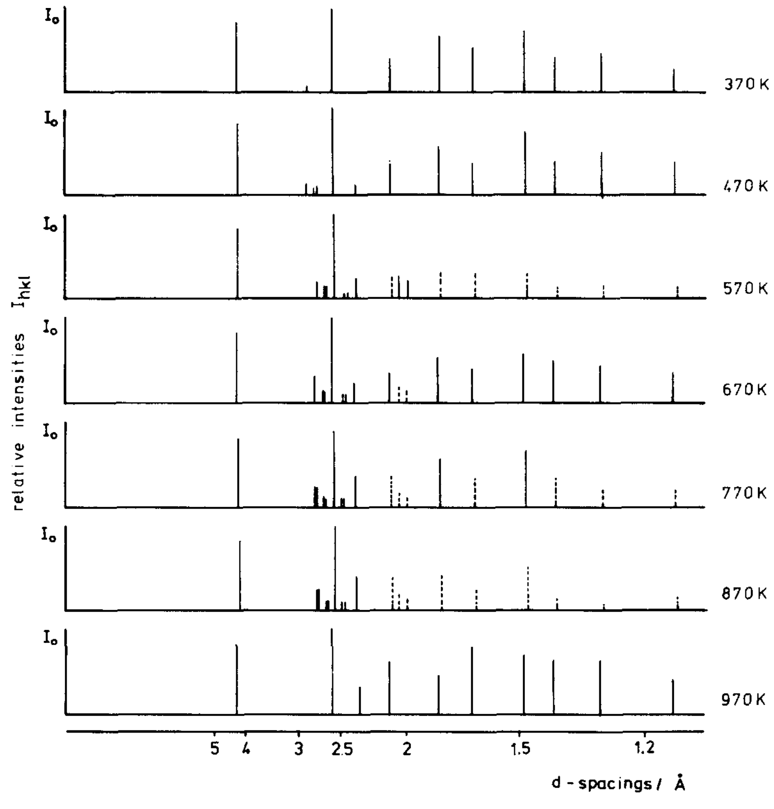


FIG. 7. Guinier powder diffraction patterns of annealed samples of $\mathrm{(Na_2O)_{0.33}Na[AlSiO_4]}$: $\mathrm{Cu}K_{\alpha_1}$ film data, relative intensities from densitometry, and broken lines for diffuse reflections. Samples prepared at 1050 K in closed systems and annealed at the lower temperatures given for 200 hr after cooling to room temperature and reheating show different but related diffraction patterns. Additional reflections having superstructure characteristics and some diffuse character in the main reflections indicate complex ordering of interstitial Na/O atoms and possibly corresponding framework interactions, respectively. Identification of these patterns is subject to further studies based either on single crystal intensities or on powder pattern profile fitting procedures.

TABLE I

POWDER DIFFRACTION DATA OF "HOST LATTICE" HIGH-CARNEGIEITE $Na[AlSiO_4]$ AT 1020 K (a = 7.301(5) Å) AND INTERCALATION COMPOUND $(Na_2O)_{0.33}[NaAlSiO_4]$ AT ROOM TEMPERATURE (a = 7.3209(1) Å)

	$Na[AlSiO_4]$/1020 K			$(Na_2O)_{0.33}[NaAlSiO_4]$/290 K		
$h\ k\ l$	d_{obs}	d_{calc}	I/I_0	d_{obs}	d_{calc}	I/I_0
1 1 1	4.19	4.22	100	4.23	4.23	76
2 0 0	3.64	3.65	2	3.65	3.66	2
2 2 0	2.58	2.58	65	2.58	2.59	100
3 1 1	2.199	2.201	5	—		—
2 2 2	2.106	2.108	10	2.112	2.113	7
4 0 0	1.824	1.825	7	1.830	1.830	13
3 3 1	1.675	1.675	9	1.679	1.680	7
4 2 0	1.632	1.633	2	—		—
4 2 2	1.489	1.490	20	1.494	1.494	31
5 1 1/333	1.405	1.405	8	1.409	1.409	5
4 4 0	1.290	1.291	5	1.294	1.294	5
5 3 1	1.234	1.234	4	—		—
6 2 0	1.154	1.155	3	1.158	1.158	6

Note. Guinier-Cu$K\alpha_1$-film data; relative intensities I/I_0 are from densitometry.

on positions $4b/4c$ of space group $F\bar{4}3m$ and allowing for reasonable thermal movements ($b \sim 4$ Å^2) lead to no considerable conflict with observed intensity data from Guinier high-resolution CuK_{α_1} diffractometry. Contrary to the choice of space group $P2_13$ of high-carnegieite $Na[AlSiO_4]$ (*6*) we favor the F-lattice-type of space group $F\bar{4}3m$ to correspond to the aristo-structure types diamond or high-cristobalite, which have space group $Fd3m$ (Fig. 5).

Thermoanalytical studies on Na_2O intercalated carnegieite phases $(Na_2O)_nNa[AlSiO_4]$ showed thermal release of intercalated nNa_2O unambiguously at temperatures >1350 K under open system conditions (Fig. 6). Na_2O effusion stops as soon as the host lattice composition of $Na[AlSiO_4]$ is reached. This material is known to melt congruently at 1800 K (*7*).

Unfortunately, we were not successful in single crystal growing experiments. None of the above techniques provided chemically homogeneous grain sizes (>10 μm) of phases $(Na_2O)_{\leq 0.33}Na[AlSiO_4]$ as revealed from microprobe-Si(K_{α_1})-scanning data or polarization microscopy. On the other hand, any further discussion, especially on the order/disorder phenomena which are strongly suggested from superstructure patterns found for annealed phases (Fig. 7), appears to be meaningless until we obtain single crystal intensity data.

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