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## Structure of the Luminescent System $\text{Na}^+/\text{UO}_2^{2+}$ $\beta''$ -Alumina

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### Abstract

The structure and ionic distribution of  $\text{Na}^+$   $\beta''$ -alumina with  $\sim 12\%$  of the sodium ions exchanged for the luminescent molecular uranyl ion ( $\text{UO}_2^{2+}$ ) has been investigated at room temperature by single-crystal X-ray diffraction. The idealized formula for the crystal studied is  $(\text{UO}_2)_y\text{-Na}_{1+x-2y}\text{Mg}_x\text{Al}_{11-x}\text{O}_{17}$ , with  $x = \frac{2}{3}$  and  $y = 0.10$ ,  $M_r = 627.8$ . The structure has the trigonal space group  $R\bar{3}m$ ,  $a = 5.6206$  (3),  $c = 33.703$  (5) Å,  $V = 922.3$  (2) Å<sup>3</sup>,  $Z = 3$ ,  $D_x = 3.39$  Mg m<sup>-3</sup>,  $\mu_{\text{obs}} = 2.03$ ,  $\mu_{\text{calc}} = 2.30$  mm<sup>-1</sup>. Spinel-type blocks comprising  $\text{Al}^{3+}$  ions, tetrahedrally and octahedrally coordinated by  $\text{O}^{2-}$  ions, are separated at  $z = \frac{1}{6}$ ,  $\frac{1}{2}$  and  $\frac{5}{6}$  by conduction planes containing  $\text{Na}^+$  and  $\text{UO}_2^{2+}$  ions and the column O atoms, O(5). These serve to hold together the spinel blocks through Al—O(5)—Al bonds. The  $\text{Mg}^{2+}$  ions stabilize the structure by substituting for one third of the  $\text{Al}^{3+}$  ions at Al(2) sites close to the centre of the spinel block ( $z \approx 0$ ). The linear  $\text{UO}_2^{2+}$  ions (length  $\sim 3.4$  Å) arrange themselves in a disordered manner in the almost two-dimensional honeycomb-shaped pathways in the conduction planes, such that the molecules straddle the 6(c)-site intersections of the pathways. The uranium atoms occupy 18(h) sites, close to the Beevers–Ross (BR) 6(c) site, and the two uranyl O atoms occupy general 36(i) sites. The sodium ions occupy either BR sites or 18(h) sites, relaxed towards adjacent BR sites. Final  $R(F) = 0.0252$ ,  $R(F^2) = 0.0371$ ,  $wR(F^2) = 0.0407$  for refinement on 2833 reflections.

### Introduction

Sodium  $\beta''$ -alumina is a solid electrolyte exhibiting an unique ion-exchange chemistry, whereby a large number of mono-, di- and trivalent cations, as well as some protonic molecular ion species can be incorporated into the conduction planes. Many of the resulting materials are of clear technological interest, the most fascinating, perhaps, being their potential use in solid-state optical devices (Dunn, Farrington & Thomas, 1989).

This almost universal ion-exchange capability is made possible through the open-layered structure of  $\beta''$ -alumina. Compact spinel-type blocks of  $\text{Al}^{3+}$  and  $\text{O}^{2-}$  ions are separated by Al—O(5)—Al bridging bonds. It is within the almost two-dimensional layers so formed that  $\text{Na}^+$  ions are situated and the  $\text{Na}^+$  mobility can occur. It is therefore into these open regions that the various ionic species exchange. Schematic representations of the structure, with its honeycomb-shaped conduction paths, are shown in Fig. 1. In  $\text{Na}^+$   $\beta''$ -alumina, sodium ions occupy, on average, five out of six of the so-called Beevers–Ross (BR) sites (see Fig. 1b). This situation, with both crystalline [spinel blocks and O(5)] and disordered 'liquid-like' regions (conduction planes), complicates the interpretation of the space- and time-averaged crystallographic picture obtained.

This paper presents a structural investigation of an  $\text{Na}^+$   $\beta''$ -alumina single crystal in which  $\sim 12\%$  of the sodium ions have been substituted for uranyl ions,  $\text{UO}_2^{2+}$ . These are molecular ions possessing a

rich photochemistry. The luminescent emission associated with  $\text{UO}_2^{2+}$  ions has been observed to be sensitive to the local environment, both in terms of line-shape and wavelength maxima (Brittain & Perry, 1980; Reisfelt, Eyal & Jørgensen, 1986). This feature suggested the use of the uranyl ion as a probe of the environment in  $\beta''$ -alumina (Hollingsworth, Zink, Barrie & Dunn, 1987); these authors also proposed a possible position of the ion in the conduction plane.

A rigorous diffraction study to determine the site(s) actually occupied by the uranyl ions is so far lacking, however.

### Experimental

Single crystals of  $\text{Na}^+$   $\beta''$ -alumina were grown by a flux evaporation technique (Briant & Farrington, 1980). The ion exchange was achieved by immersing these crystals in a sodium nitrate ( $\text{NaNO}_3$ ) melt containing an appropriate amount of uranyl nitrate [ $\text{UO}_2(\text{NO}_3)_2$ ] at 623 K for 2–18 h. The single crystal from which the crystal used for the diffraction study was subsequently removed was further subjected to microprobe analysis. Taking  $\text{O}_{17}$  as standard gave the composition  $(\text{UO}_2)_{0.10(2)}\text{Na}_{1.47}\text{Mg}_{0.66(2)}\text{Al}_{10.36(8)}\text{O}_{17}$  (no reliable sodium analysis was possible; sodium content was therefore constrained to maintain charge balance).

The crystal used for the intensity measurements had maximum/minimum dimensions 0.35/0.08 mm. Intensity data were collected on a computer-controlled automatic Stoe four-circle diffractometer using graphite-monochromatized  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and an  $\omega/2\theta$  step scan. A preliminary data collection was made in the range  $15 \leq 2\theta \leq 30^\circ$ , in which no reflections other than those of the type  $-h + k + l = 3n$  could be observed, thus confirming the accuracy of the trigonal space-group assignment. This indexing condition (within a hexagonal indexing scheme) was then used for the data collection, which proceeded for reflections  $h, k, \pm l$  out to  $\sin\theta/\lambda = 1.13 \text{ \AA}^{-1}$ .

Five standard reflections were chosen to monitor the stability of the diffractometer and the crystal. The systematic decrease in intensity displayed by these reflections was used to correct the entire data set. Correction for absorption was made using an explicit description of the crystal and a value for the linear absorption coefficient obtained by measuring absorption in the original crystal ( $\mu_{\text{obs}} = 2.03 \text{ mm}^{-1}$ ). The measured intensity profiles were further corrected for background using the Lehmann-Larsen method (Lehmann & Larsen, 1974); an Lp correction was also made. The experimental parameters are summarized in Table 1, together with some of the parameters used in the refinements.

### Refinement

Refinements based on the complete data set were made using the full-matrix least-squares program *DUPALS* (Lundgren, 1982) in which the function minimized was  $\sum w(|F_o^2| - |F_c^2|)$  where  $w^{-1} = \sigma^2(F_o^2) = \sigma_c^2(F_o^2)^2 + (kF_o^2)^2$ ;  $\sigma_c$  = estimated standard deviation based on Poisson counting statistics;  $k$  is

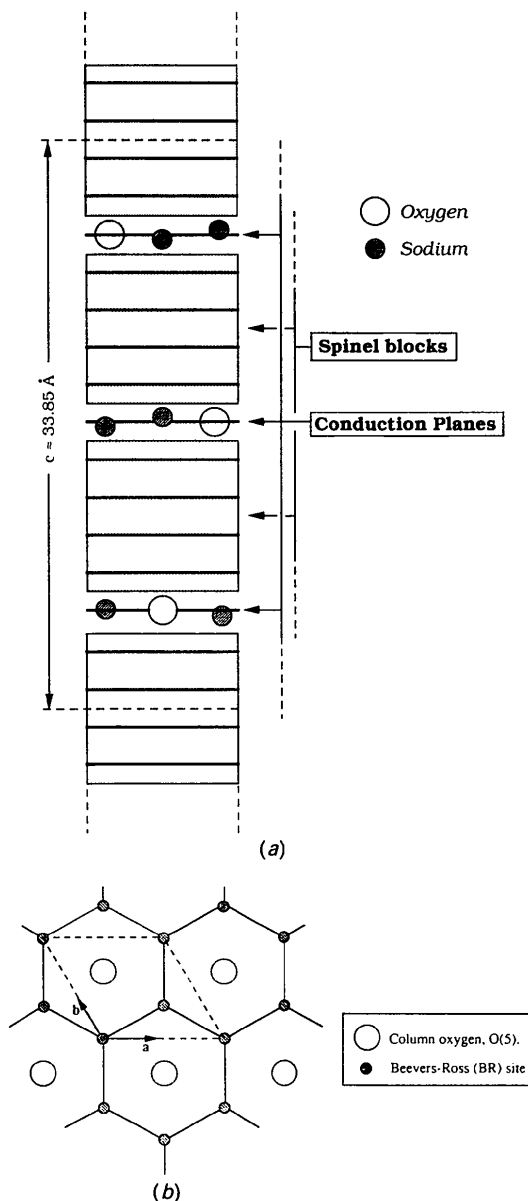


Fig. 1. Schematic representation of the structure of  $\text{Na}^+$   $\beta''$ -alumina showing (a) the overall block structure and (b) the conduction plane at  $z = \frac{1}{6}$  with its honeycomb-shaped conduction paths. The unit-cell (dashed) and Beavers-Ross (BR) sites are indicated.

Table 1. *Experimental parameters*

Diffractometer	Stoe four-circle
Radiation	Mo Kα (λ = 0.71073 Å)
Temperature (K)	295
Scan type	ω/2θ
F(000)	915.9
Cell parameters a, c (Å)	5.6206 (3), 33.703 (5)
No. of reflections for cell determination (2θ interval)	20 (15–30°)
Cell volume (Å <sup>3</sup> )	922.3 (2)
D <sub>r</sub> (Mg m <sup>-3</sup> )	3.39
Crystal dimensions (mm)	0.35 × 0.27 × 0.08
μ <sub>obs</sub> , μ <sub>calc</sub> (mm <sup>-1</sup> )	2.03, 2.30
Transmission factors	0.70–0.93
(sinθ/λ) <sub>max</sub> (Å <sup>-1</sup> )	1.13
h, k, l range	0 ≤ h ≤ 10, 0 ≤ k ≤ 10, -75 ≤ l ≤ 75
No. of standards	5
No. of observed reflections	3119
No. of unique reflections	1430
No. of reflections excluding zero weight [I ≤ 2σ(I)]	2833
R <sub>int</sub> = Σ I <sub>o</sub> - I <sub>c</sub>  /ΣI <sub>o</sub>	0.016
Max./min. in final difference map (e Å <sup>-3</sup> )	0.34/-0.55
No. of parameters refined	56
R(F <sub>o</sub> )	0.0252
R(F <sub>c</sub> <sup>2</sup> )	0.0371
wR(F <sub>c</sub> <sup>2</sup> )	0.0407
S	1.10
Δσ <sub>max</sub>	0.005

an empirical constant, here set to 0.02. Reflections with  $F^2 \leq 2\sigma(F^2)$  were removed from the data set, leaving 2833 reflections for the final refinement. The coherent-scattering amplitudes and anomalous-scattering terms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Assuming the structure of the spinel framework to be insignificantly different from that of Na<sup>+</sup> β''-alumina (Bettman & Peters, 1969), the published positions for the crystalline framework [spinel block and O(5)] were used as start parameters. An initial difference Fourier map in the  $z = \frac{1}{2}$  plane gave a crude picture of the cation distribution in the conduction plane. Most residual electron density is concentrated at and around the BR sites. A model, assuming intact disordered UO<sub>2</sub><sup>2+</sup> ions (O—O distance ≈ 3.4 Å) is shown schematically in Fig. 2. With sodium ions also occupying BR sites, the electron-density map represents a superposition of UO<sub>2</sub><sup>2+</sup> and Na<sup>+</sup> ions. There was also some suggestion that the column O atoms, O(5), are displaced from the 3(b) centrosymmetric site. It is reasonable that the uranyl oxygen ions, O(6), should interact electrostatically with O(5), thereby forcing them out of their 3(b) sites into 18(g) sites (Fig. 2). The distance between O(6) and the mean O(5) position is 2.251 (3) Å. Depending on the degree of exchange and the nature of the dopant, this interaction generally results in a bending of the Al—O(5)—Al bond and hence a contraction of the *c* axis. The effect is quite small here: the *c* axis is ~0.15 Å shorter than in Na<sup>+</sup> β''-alumina. The essential features of the final refinement can be summarized as follows:

(i) The UO<sub>2</sub><sup>2+</sup> ion, involving covalent U—O bonds, was described as a U<sup>6+</sup> and two O<sup>2-</sup> ions.

(ii) The ion was treated as a rigid linear molecule, *i.e.* the oxygen ions were constrained to follow the

movement of the uranium ion with the uranium at an 18(*h*) site and the oxygen ions at 36(*i*) sites.

(iii) The uranyl content was held fixed to the value obtained from the microprobe analysis (corresponding to 12% sodium ions exchanged).

(iv) The sodium distribution was described using two site types: BR [6(*c*)] sites [Na(BR)] and 18(*h*) sites [Na(2)] displaced along the conduction paths toward adjacent BR sites.

(v) The Na<sup>+</sup> content, though fixed initially to 1.47 to give charge balance, was refined freely in the final refinement to yield an improved agreement factor and a total charge of 1.72 (8).

(vi) The column O atom was best described using a six disordered 18(*g*) site, displaced 0.12 Å from the 3(*b*) site.

(vii) Anisotropic temperature factors (β<sub>*ij*</sub>'s) were used for all ions.

(viii) The occupancies for the ions forming the structural framework were fixed to values corresponding to the ideal composition, *i.e.* Mg<sub>0.67</sub>Al<sub>10.33</sub>O<sub>17</sub>, with no attempt made to represent the Mg<sup>2+</sup> ions explicitly, since their X-ray form factor is so similar to that of Al<sup>3+</sup>.

An isotropic extinction coefficient was refined to a *g* value of 2.9 (3) × 10<sup>3</sup> (Becker & Coppens, 1974). Refined positional parameters, occupancies and displacement parameters are given in Table 2. The final observed (*F*<sub>o</sub>) syntheses at  $z = \frac{1}{2}$  are plotted in Fig. 3, while some cation–oxygen distances are given in Table 3. Observed and calculated structure factors have been deposited together with selected interatomic distances and angles.\* Final agreement factors were  $R(F^2) = 0.0371$ ,  $wR(F^2) = 0.0407$ , and the conventional  $R(F) = 0.0252$ .

\* Lists of harmonic and anharmonic atomic displacement parameters, interatomic distances and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55928 (59 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB0295]

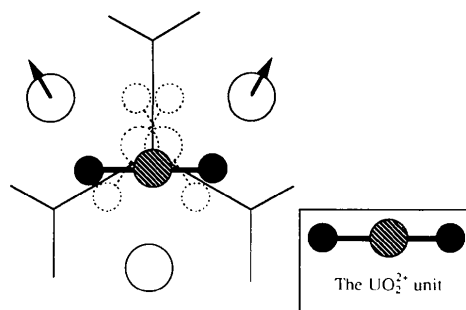


Fig. 2. Schematic model for the uranyl ions in the conduction plane. The electrostatic repulsion acting upon the O(5) atoms is indicated by arrows.

Table 2. Fractional coordinates, occupancies (expressed as fractional site occupations and as number of ions per formula unit) and isotropic displacement parameters (expressed as mean-square amplitudes)

$$U_{\text{eq}} = (U_{11} + U_{22} + U_{33})/3.$$

Ion	Site	x	y	z	Site occupancy	Atoms per formula unit	$U_{\text{eq}} \times 10^{-3}$ (Å <sup>2</sup> )
U	18(h)	-0.0672 (4)	x/2	0.17210 (5)	0.016 (3)	0.10 (2)*	9.8
O(6)	36(i)	-0.0672 (4)	0.2689 (2)	0.17210 (4)	0.016 (3)	0.20 (4)*	9.8
Na(BR)	6(c)	0	0	0.166 (2)	0.15 (2)	0.29 (4)	259
Na(2)	18(h)	0.141 (2)	x/2	0.1707 (1)	0.238 (6)	1.43 (4)	146
A1(1)	3(a)	0	0	0	1.0	1.0	4.3
A1(2)	6(c)	0	0	0.35017 (1)	1.0	2.0	5.1
A1(3)	18(h)	0.33429 (3)	x/2	0.07094 (1)	1.0	6.0	4.8
A1(4)	6(c)	0	0	0.44999 (1)	1.0	2.0	4.2
O(1)	18(h)	0.15391 (4)	2x	0.03431 (1)	1.0	6.0	7.2
O(2)	6(c)	0	0	0.29513 (2)	1.0	2.0	6.2
O(3)	6(c)	0	0	0.09706 (2)	1.0	2.0	6.1
O(4)	18(h)	0.16331 (4)	2x	0.23521 (1)	1.0	6.0	6.0
O(5)	18(g)	0.291 (4)	‡	‡	‡	1.0	24.1

\* Value fixed to that obtained from a microprobe analysis.

Table 3. Selected U—O and Na—O distances (Å) in Na<sup>+</sup>/UO<sub>2</sub><sup>2+</sup> β''-alumina

	Multiplicity	Distance
U—O(6)*	(× 2)	1.700
U—O(5)	(× 1)	2.72 (4)
U—O(4)	(× 2)	2.473 (2)
U—O(3)	(× 1)	2.550 (2)
O(6)—O(5)	(× 1)	2.49 (5)
Na(BR)—O(5)	(× 3)	3.04 (4)
Na(BR)—O(4)	(× 3)	2.81 (4)
Na(BR)—O(3)	(× 1)	2.34 (5)
Na(2)—O(5)	(× 2)	2.74 (5)
Na(2)—O(4)	(× 2)	2.575 (3)
Na(2)—O(3)	(× 1)	2.576 (5)

\* Fixed value.

### Discussion

The spinel-block structure is essentially the same as found in other β''-aluminas studied (see, for example, Dunn, Farrington & Thomas, 1989, and references therein) and will not be discussed in any greater detail here. The main feature of structural interest is the ionic arrangement in the disordered conduction planes. Here, the two cations (Na<sup>+</sup> and UO<sub>2</sub><sup>2+</sup>) partially occupy almost coincident BR sites: the Na<sup>+</sup> (BR) ion is refined to  $z = 0.167$  (2), *i.e.* exactly in the conduction plane, instead of undulating as it normally does from  $\sim 0.2$  Å above to  $\sim 0.2$  Å below the conduction plane (corresponding to a  $z$  value of  $\sim 0.172$ ). Moreover, the description of the sodium distribution also requires a second site [18(h)] to take account of the dominant part of the sodium occupation. These complications may have influenced the total occupation number for sodium: artificially high occupation is indeed a common feature in models of such extended sodium-ion distributions.

The treatment of the UO<sub>2</sub><sup>2+</sup> ion as a linear molecule would seem justified. The scattering from the uranyl oxygen ions, O(6), is somewhat difficult to

detect because of the combination of low concentration, poor scattering power and orientational disorder in the conduction plane. Nevertheless, the electron-density contribution from O(6) can be clearly identified in a difference Fourier synthesis (Fig. 4).

The original motivation for incorporating UO<sub>2</sub><sup>2+</sup> into the structure was to study the luminescence spectra and optical lifetimes for the UO<sub>2</sub><sup>2+</sup> ion in the environment of the β''-alumina framework. It was concluded that the optical spectrum for UO<sub>2</sub><sup>2+</sup> consisted of a superposition of spectra for ions in at least two different environments. Moreover, the widths of the peaks indicated that there was significant local disorder at each site (Hollingsworth, Zink, Barrie & Dunn, 1987). Although diffraction studies of mobile-ion systems are limited in their ability to determine short-range-order effects (Thomas, 1992), it is possible to gain at least some idea as to how the 'real'

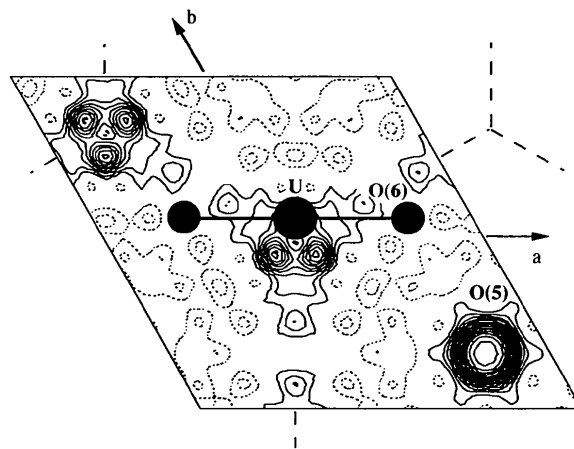


Fig. 3. Final  $F_{\text{obs}}$  syntheses at  $z = \frac{1}{6}$  (the conduction plane). Contour interval:  $1.5 e \text{ \AA}^{-3}$ .

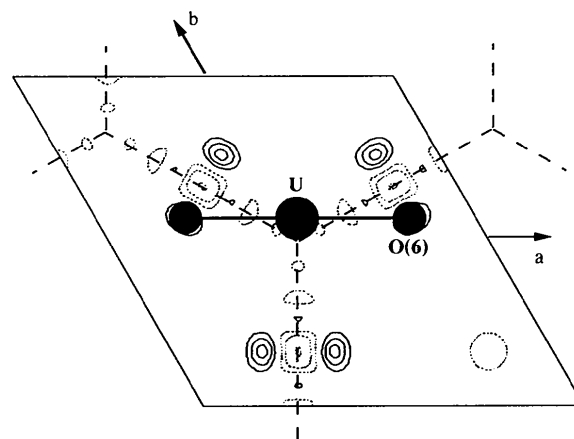


Fig. 4. Difference synthesis calculated at  $z = 0.172$  excluding the oxygen atoms of the UO<sub>2</sub><sup>2+</sup> ion. Contour interval:  $0.2 e \text{ \AA}^{-3}$ .

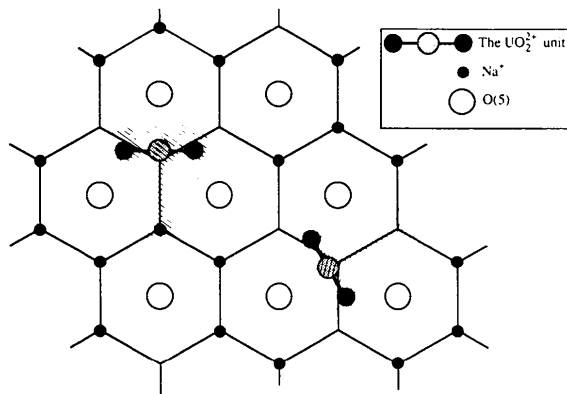


Fig. 5. Two possible environments for the UO<sub>2</sub><sup>+</sup> unit in the conduction plane.

local situation may be on the basis of occupations and electrostatic considerations. The two distinctly different environments for the UO<sub>2</sub><sup>+</sup> ions suggested by the optical spectrum are likely to be those with and without Na<sup>+</sup> as a nearest neighbour (see Fig. 5). There can be several sources for the lack of homogeneity associated with a given site, e.g., the UO<sub>2</sub><sup>+</sup> ion can be slightly tilted, it can be influenced by next-nearest-neighbour Na<sup>+</sup> ions, or a second uranyl ion can occupy a nearby site. It is clear, however,

that the structural picture presented here is fully consistent with the appearance of the luminescence spectrum.

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## Modulation Wave Approach to the Structural Parameterization and Rietveld Refinement of Low Carnegieite

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### Abstract

The crystal structure of low carnegieite, NaAlSiO<sub>4</sub> [ $M_r = 142.05$ , orthorhombic,  $Pb2_1a$ ,  $a = 10.261(1)$ ,  $b = 14.030(2)$ ,  $c = 5.1566(6)$  Å,  $D_x = 2.542$  g cm<sup>-3</sup>,  $Z = 4$ , Cu  $K\alpha_1$ ,  $\lambda = 1.5406$  Å,  $\mu = 77.52$  cm<sup>-1</sup>,  $F(000) = 559.85$ ], is determined *via* Rietveld refinement from powder data,  $R_p = 0.057$ ,  $R_{wp} = 0.076$ ,  $R_{Bragg} = 0.050$ . Given that there are far too many parameters to be determined *via* unconstrained Rietveld refinement, a group theoretical or modulation wave approach is used in order to parameterize the structural deviation of low carnegieite from its underlying C9 aristotype. Appropri-

ate crystal chemical constraints are applied in order to provide two distinct plausible starting models for the structure of the aluminosilicate framework. The correct starting model for the aluminosilicate framework as well as the ordering and positions of the non-framework Na atoms are then determined *via* Rietveld refinement. At all stages, chemical plausibility is checked *via* the use of the bond-length–bond-valence formalism. The JCPDS file number for low carnegieite is 44-1496.

### 1. Introduction

Carnegieite, NaAlSiO<sub>4</sub>, is one of a large family of materials topologically closely related to the so-called C9 structure type (O'Keeffe & Hyde, 1976). Its parent

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