

phosphite groups on the threefold axis gave either unstable refinements or chemically unreasonable structures, hence all were left in the same orientation as in the Fe compound.

MPA would like to acknowledge the University of California, Santa Barbara, for the provision of a scholarship.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry for Fe<sub>11</sub>(HPO<sub>3</sub>)<sub>8</sub>(OH)<sub>6</sub>, and primary powder diffraction data and H-atom coordinates for Mn<sub>11</sub>(HPO<sub>3</sub>)<sub>8</sub>(OH)<sub>6</sub> have been deposited with the IUCr (Reference: BR1071). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Rietveld Refinement of Dry-Synthesized Rb<sub>2</sub>ZnSi<sub>5</sub>O<sub>12</sub> Leucite by Synchrotron X-ray Powder Diffraction

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### Abstract

Analysis of a high-resolution synchrotron X-ray powder diffraction pattern of a dry-synthesized rubidium zinc silicate, leucite analogue Rb<sub>2</sub>ZnSi<sub>5</sub>O<sub>12</sub>, showed that this material has a cubic *la3d* structure. The structure of this material has been refined by the Rietveld method. Si and Zn

atoms are disordered on tetrahedral framework sites and Rb occupies large channel sites along the [111] direction.

### Comment

As part of a wider attempt to understand the controls and consequences of tetrahedral-cation ordering, we are studying a series of synthetic leucite analogues X<sub>2</sub>Z<sup>II</sup>Si<sub>5</sub>O<sub>12</sub> (X = K, Rb, Cs; Z = Mg, Zn, Cd) in silicates with framework structures related to natural leucite (KAlSi<sub>2</sub>O<sub>6</sub>) by the coupled framework cation substitution 2Al = Z, Si (Torres-Martinez & West, 1989). Such compounds are more amenable to tetrahedral site (*T*-site) analysis than Al/Si analogues and also display significantly different *T*-site ordering arrangements depending on their conditions of synthesis and chemical compositions.

X-ray powder diffraction techniques and Rietveld analysis (Rietveld, 1969) were used to determine the crystal structures of these materials, together with <sup>29</sup>Si magic-angle spinning NMR spectroscopy, to characterize the number of distinct Si sites. Some of the leucite analogues we have studied have known leucite-type structures, but we have also determined previously unknown monoclinic (*P2<sub>1</sub>/c*; Bell, Henderson, Redfern, Cernik, Champness, Fitch & Kohn, 1994) and orthorhombic (*Pbca*; Bell, Redfern, Henderson & Kohn, 1994) structures which have the basic leucite topology. In this paper we describe the structure of a dry-synthesized leucite with the stoichiometry Rb<sub>2</sub>ZnSi<sub>5</sub>O<sub>12</sub>.

Analysis of the powder diffraction data showed (from the systematic absences) that this material has a cubic *la3d* structure. Therefore, atomic coordinates for the *la3d* structure of dry-synthesized K<sub>2</sub>MgSi<sub>5</sub>O<sub>12</sub> (Bell, Henderson, Redfern, Cernik, Champness, Fitch & Kohn, 1994) were used as a starting model for Rietveld refinement. The Rb<sub>2</sub>ZnSi<sub>5</sub>O<sub>12</sub> structure was then refined using the *MPROF* program of the *Powder Diffraction Program Library (PDPL)* (Murray, Cockcroft & Fitch, 1990). The observed and calculated profiles in the Rietveld difference plot were a good match (Fig. 1) indicating that the refined structure is reliable.

The *la3d* structure is characterized by having a single *T* site and the tetrahedral cations must be disordered on this site. Thus the leucite-group natural mineral, pollucite (CsAlSi<sub>2</sub>O<sub>6</sub>; Beger, 1969), has disordered Si and Al arrangements, while dry-synthesized Rb<sub>2</sub>ZnSi<sub>5</sub>O<sub>12</sub> has disordered Si and Zn. Other synthetic leucites are also cubic *la3d* (Bell, Henderson, Redfern, Cernik, Champness, Fitch & Kohn, 1994; Torres-Martinez & West, 1989) with similarly disordered tetrahedral cations.

The refined *T*—O distances of the title compound represent the weighted average of tetrahedrally coordinated Si—O and Zn—O bond lengths of the disordered framework. The distortions in the framework structure resulting from the presence of Zn in *T* sites are also reflected in the range of O—*T*—O angles of 103–113° [cf. 102–119° in dry-synthesized Rb<sub>2</sub>MgSi<sub>5</sub>O<sub>12</sub> (Torres-Martinez

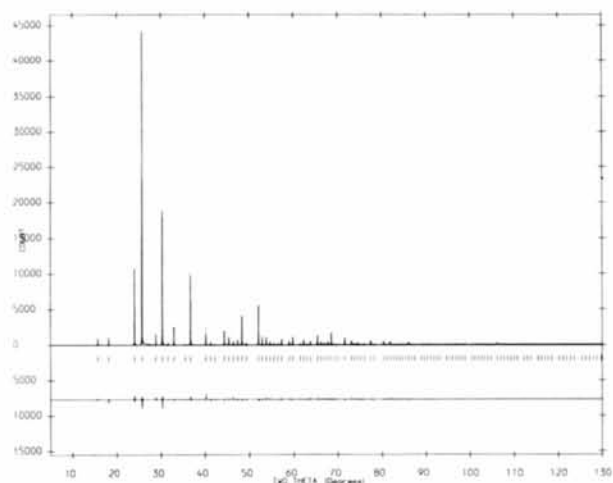


Fig. 1. Rietveld difference plot for dry-synthesized  $\text{Rb}_2\text{ZnSi}_5\text{O}_{12}$ .

& West, 1986)]. The Rb cations occupy large interstitial sites in the structure (Fig. 2) accounting for the long Rb—O bond lengths. Note that the values obtained for  $1a\bar{3}d$   $\text{Rb}_2\text{ZnSi}_5\text{O}_{12}$  leucite are similar to those obtained for K—O in  $\text{K}_2\text{MgSi}_5\text{O}_{12}$  [3.34 and 3.47 Å (Bell, Henderson, Redfern, Cernik, Champness, Fitch & Kohn, 1984)], Rb—O in  $\text{Rb}_2\text{MgSi}_5\text{O}_{12}$  [3.29 and 3.60 Å (Torres-Martinez & West, 1986)] and Cs—O in natural pollucite [3.39 and 3.56 Å (Beger, 1969)]. The displacement parameters for all atom species in these materials are uniformly high, reflecting the disorder of the tetrahedral cations on the T sites, the disordered nature of O-atom positions associated with the random arrangement of T cations, and the static

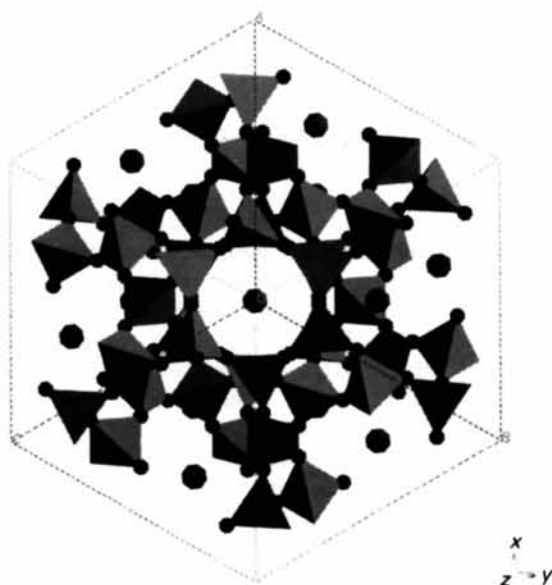


Fig. 2. Projection of the structure of  $\text{Rb}_2\text{ZnSi}_5\text{O}_{12}$  along [111]. Tetrahedra represent  $\text{TO}_4$  units, large circles represent  $\text{Rb}^+$  cations and small circles represent  $\text{O}^{2-}$  anions.

and thermal disorder of the alkali cations in the distorted large channel sites along [111] in the framework. It is possible that the presence of weakly bonded alkali cations in these large channels could lead to these materials being fast-ion conductors.

## Experimental

Appropriate portions of  $\text{Rb}_2\text{CO}_3$ ,  $\text{ZnO}$  and  $\text{SiO}_2$  were mixed and melted at 1523 K for 24 h in a platinum crucible, then cooled by dipping into liquid nitrogen to form a glass, which was heated at 1123 K for 5 d to produce the dry-synthesized sample.

### Crystal data

$\text{Rb}_2\text{ZnSi}_5\text{O}_{12}$

$M_r = 568.74$

Cubic

$1a\bar{3}d$

$a = 13.4972(1) \text{ \AA}$

$V = 2458.86(3) \text{ \AA}^3$

$Z = 8$

$D_x = 3.07 \text{ Mg m}^{-3}$

Synchrotron radiation

$\lambda = 1.5044 \text{ \AA}$

$\mu = 18.0 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Powder

Sample mounted in reflection mode

### Data collection

High-resolution powder

diffractometer, SRS

station 8.3 (Cernik,

Murray, Pattison &

Fitch, 1990)

Parallel beam non-focusing

optics with channel-

cut monochromator and

scintillation detector

Method for scanning reciprocal

space: step scan

Absorption correction

method: none

12 501 data points measured

12 501 data points in the

processed diffractogram

$2\theta_{\min} = 5.00$ ,  $2\theta_{\max} =$

$130.00^\circ$

Increment in  $2\theta$   $0.01^\circ$

### Refinement

$R_{wp}(\text{obs.}) = 0.1389$  (Young,

Prince & Sparks, 1982)

$R_{wp}(\text{calc.}) = 0.1119$

$R_I = 0.0775$  (Young, Prince

& Sparks, 1982)

$S = 1.5417$

192 reflections

15 parameters

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV, Table

2.3.1)

Table 1. Fractional atomic coordinates, isotropic displacement parameters ( $\text{\AA}^2$ ) and occupancy factors

|    | x          | y           | z          | $U_{\text{iso}}$ | Occupancy |
|----|------------|-------------|------------|------------------|-----------|
| Rb | 1/8        | 1/8         | 1/8        | 5.90 (3)         | 1.000     |
| Si | 1/8        | 0.66294 (8) | $5/4 - y$  | 3.27 (3)         | 0.833     |
| Zn | 1/8        | 0.66294 (8) | $5/4 - y$  | 3.27 (3)         | 0.167     |
| O  | 0.1462 (2) | 0.3857 (2)  | 0.1462 (2) | 7.07 (9)         | 1.000     |

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

|               |            |           |               |            |           |
|---------------|------------|-----------|---------------|------------|-----------|
| Si/Zn—O'      | $\times 2$ | 1.658 (3) | Rb—O          | $\times 6$ | 3.492 (2) |
| Si/Zn—O''     | $\times 2$ | 1.589 (3) | Rb—O          | $\times 6$ | 3.352 (2) |
| O'—Si/Zn—O''  |            | 113.2 (1) | O''—Si/Zn—O'  |            | 113.2 (1) |
| O'—Si/Zn—O''  |            | 110.3 (1) | O''—Si/Zn—O'  |            | 110.3 (1) |
| O'—Si/Zn—O'   |            | 103.3 (1) | Si/Zn—O—Si/Zn |            | 143.4 (2) |
| O''—Si/Zn—O'' |            | 106.7 (1) |               |            |           |

The raw synchrotron powder-diffraction data was normalized to account for the decay of the synchrotron radiation beam; the

least-squares weighting scheme for the refinement is (normalization factor/profile intensity + background). Data collection was performed with in-house software. Cell refinement and structure refinement were performed with *REFCEL* and *MPROF* of *PDPL* (Murray, Cockcroft & Fitch, 1990). *CERIUS* software (Molecular Simulations) was used for molecular graphics.

We acknowledge the use of the SERC-funded Chemical Database Service at Daresbury and also thank the SERC for the award of synchrotron beamtime. AMTB wishes to thank Brian McMahan and Mike Hoyland of the IUCr, Chester, for help in generating a CIF format for powder diffraction structures.

Lists of raw powder data and complete geometry have been deposited with the IUCr (Reference: BR1072). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Un Monophosphate de Magnésium et de Sodium

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### Abstract

The title compound, magnesium sodium phosphate, Mg<sub>5</sub>Na<sub>2</sub>(PO<sub>4</sub>)<sub>4</sub>, belongs to a group of monophosphates which are constructed from five kinds of

coordination polyhedra: two kinds of PO<sub>4</sub> tetrahedra are connected by one type of Mg–O octahedra situated at the centres of symmetry; distorted five-coordinated Mg–O polyhedra and another type of distorted Mg–O octahedra are in general positions. Na–O polyhedra occupy the cavities formed by these five types of coordination polyhedra. The density,  $D_x$ , of this compound is 3.00 Mg m<sup>-3</sup>, reflecting the high-pressure synthesis. Similar compounds precipitated at 1 atm. (101.325 kPa) have densities of 2.55–2.82 Mg m<sup>-3</sup>, corresponding to the lower pressure condition.

## Commentaire

Cette étude vise la contribution à la compréhension systématique des structures des monophosphates. Ghorbel, d'Yvoire & Dorémieux-Morin (1974) ont fait la synthèse des trois composés: MgNa<sub>4</sub>(PO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O et MgNa<sub>4</sub>(PO<sub>4</sub>)<sub>2</sub>-α et -γ. La relation structurale entre elles a été étudiée à l'aide de la diffraction des rayons X sur poudre à hautes températures. Ben Amara, Vlasse, Olazcuaga, Le Flem & Hagenmuller (1983) ont déterminé la structure de Mg<sub>4</sub>Na(PO<sub>4</sub>)<sub>3</sub>. Nous donnons dans cet article la structure d'une nouvelle phase obtenue par synthèse hydrothermale.

La densité de ce produit est 3,00 Mg m<sup>-3</sup>, nettement supérieure à 2,55–2,56 Mg m<sup>-3</sup> de MgNa<sub>4</sub>(PO<sub>4</sub>)<sub>2</sub>-α et -γ (Ghorbel *et al.*, 1974) et de 2,82 Mg m<sup>-3</sup> pour Mg<sub>4</sub>Na(PO<sub>4</sub>)<sub>3</sub> (Ben Amara *et al.*, 1983). La densité élevée de notre produit refléterait la condition de la synthèse.

Le résultat de la détermination de la structure de notre produit est illustré par une image stéréographique dans la Fig. 1 et par la représentation dans la Fig. 2. Il existe trois positions pour les atomes de Mg: Mg(1) et Mg(2) se trouvent aux positions générales et entouré respectivement de six et cinq atomes d'O. Mg(3) est situé au centres du symmétrie avec les coordinances tordues octaédriques. Ces trois sortes de polyèdres de Mg sont liés aux deux sortes de tétraèdres isolés du P en mettant en commun leurs coins des atomes d'O. Les polyèdres de Na se trouvent aux interstices des polyèdres de Mg et de P.

Les distances Mg–O moyennes correspondant aux trois sortes de Mg polyèdres sont: 2,102, 2,026 et 2,120 Å, compatible au résultat antérieur (2,023, 2,076 et 2,080 Å; Ben Amara *et al.*, 1983). Les valeurs moyennes de la distance P–O sont 1,538 et 1,535 Å pour les deux sortes de tétraèdres de PO<sub>4</sub> (1,526, 1,538 et 1,538 Å; Ben Amara *et al.*, 1983), qui sont en accord avec 1,536 Å obtenue par Corbridge (1971). Les indices de distortion  $[d(M-O)_{\max} - d(M-O)_{\min}] / \langle d(M-O) \rangle$  pour polyèdre de Mg–O sont 0,088, 0,088 et 0,138 (les résultats antérieurs: 0,071, 0,097 et 0,142) et pour les tétraèdres de PO<sub>4</sub>