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A synchrotron study of Na_{2.27}Ho_{7.73}(SiO₄)₆O_{0.72}

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Key indicators: powder synchrotron study; $T = 295$ K; mean $\sigma(\text{Si-O}) = 0.016$ Å; disorder in main residue; R factor = 0.010; wR factor = 0.14; data-to-parameter ratio = 12.8.

A well crystallized powder sample of sodium holmium orthosilicate oxyapatite, Na_{2.27}Ho_{7.73}(SiO₄)₆O_{0.72}, was obtained after mechanical milling and thermal treatment at 1123 K. Crystal structure analysis was performed from the results of Rietveld refinement of the synchrotron diffraction data. As in other rare-earth orthosilicate apatites, sodium cations appear located sharing with holmium the 4*f* Wyckoff position at the center of a tricapped trigonal prism. In its turn, holmium almost fully occupies the 6*h* position at the center of a seven-coordinated pentagonal bipyramid. A small quantity of Na atoms was found at this site. No vacancies are present in the two independent crystallographic sites available for Ho and Na atoms.

Related literature

The method of preparation was based on Rodríguez-Reyna *et al.* (2006) and Fuentes *et al.* (2006). For related structures, see: Gunawardane *et al.* (1982); Gualtieri (2000); Emirdag-Eanes *et al.* (2004); Redhammer & Roth (2003). For bond-valence parameters for oxides, see: Brese & O'Keeffe (1991).

Experimental

Crystal data

Ho_{7.73}Na_{2.27}O_{24.72}Si₆
 $M_r = 1891.09$
 Hexagonal, $P6_3/m$
 $a = 9.3405$ (1) Å
 $c = 6.7638$ (1) Å
 $V = 511.05$ (1) Å³
 $Z = 1$

Synchrotron radiation
 $\lambda = 1.033490$ (7) Å
 $T = 295$ K
 Specimen shape: flat sheet
 $15 \times 15 \times 0.2$ mm
 Specimen prepared at 1123 K

Data collection

SSRL diffractometer
 Specimen mounting: packed powder
 sample container
 Specimen mounted in reflection
 mode

Scan method: step
 $2\theta_{\min} = 5$, $2\theta_{\max} = 70.0^\circ$
 Increment in $2\theta = 0.01^\circ$

Refinement

$R_p = 0.10$
 $R_{wp} = 0.14$
 $R_{\text{exp}} = 0.11$
 $R_B = 0.04$
 $S = 1.27$
 Excluded region(s): none

Profile function: conventional
 pseudo-Voigt
 281 reflections
 22 parameters
 Preferred orientation correction:
 none

Data collection: *SSRL Software*; cell refinement: *DICVOL* (Boultif & Louër, 2004); data reduction: *FULLPROF* (Rodríguez-Carvajal, 2006); method used to solve structure: coordinates taken from an isotopic compound; program(s) used to refine structure: *FULLPROF*; molecular graphics: *ATOMS* (Dowty, 1994); software used to prepare material for publication: *ATOMS*.

Portions of this research were carried out at the Stanford Synchrotron Radiation Lightsource (<http://smb.slac.stanford.edu/powder/>), a national user facility operated by Stanford University on behalf of the US Department of Energy, Office of Basic Energy Sciences. The authors thank Manuel Aguilar for the conventional X-ray diffraction measurements at the Instituto de Física, Universidad Nacional Autónoma de México, and Carlos Linares for the WDS measurements at the Laboratorio Universitario de Petrología, Universidad Nacional Autónoma de México, and Angel Osornio for technical support. IR acknowledges a fellowship from the Consejo Nacional de Ciencia y Tecnología (CONACyT) and projects CONACyT SEP-2004-C01-47652 and DGAPA-PAPIIT IN118106-3.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2094).

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A synchrotron study of $\text{Na}_{2.27}\text{Ho}_{7.73}(\text{SiO}_4)_6\text{O}_{0.72}$

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S1. Comment

Apatites with general formula $M_{10}(\text{XO}_4)_6\text{Z}_2$ commonly have cationic and anionic substitutions generating different structural arrangements. In the preceding chemical formula, M is a divalent atom (typically Ca^{2+} and others); Z represents F, OH, Br, Cl or O^{2-} ; while X frequently is P^{5+} and in some cases Si^{4+} , Ge^{4+} or V^{4+} . Most apatites crystallize in the hexagonal system with symmetry given by the space group $\text{P6}_3/m$ (No.176). Charge balance is assured by the presence of point defects or cationic vacancies in cases in which the element M splits in M' and M'' being M' an alkaline monovalent ion and M'' a trivalent metal giving rise to $M'_xM''_{10-x}(\text{SiO}_4)_6\text{O}_{3-x}$ oxyapatites, as in $\text{NaNd}_9(\text{GeO}_4)_6\text{O}_2$ (Emirdag-Eanes *et al.*, 2004) and $\text{LiY}_9(\text{SiO}_4)_6\text{O}_2$ (Redhammer & Roth, 2003). The structural data used for the title OAp phase was established considering the isostructural compound $\text{NaY}_9(\text{SiO}_4)_6\text{O}_2$ reported by Gunawardane *et al.* (1982). For this compound, the chemical formula $\text{Na}_x\text{Y}_{10-x}(\text{SiO}_4)_6\text{O}_2$ represents a model in which the sodium ion is introduced in the apatite structure substituting for yttrium. In the present work the nominal formula used for holmium oxyapatite and the possible incorporation of sodium and fluorine is represented as $\text{Na}_x\text{Ho}_{10-x}(\text{SiO}_4)_6\text{O}_{2-y}\text{F}_y$. The crystal structure of OAp has an arrangement similar to some other alkaline rare-earth oxyapatites already reported such as $\text{NaY}_9(\text{SiO}_4)_6\text{O}_2$ and $\text{LiY}_9(\text{SiO}_4)_6\text{O}_2$ (Redhammer & Roth, 2003).

S2. Experimental

The mechanical milling at 612 rpm (FRITSCH Pulverisette mill model 06.102) of sodium holmium orthosilicate oxyapatite (OAp) was carried out considering the nominal composition $\text{Na}_2\text{Ho}_8(\text{SiO}_4)_6\text{F}_2$ from stoichiometric mixtures of Ho_2O_3 (Aldrich.99.9%), SiO_2 (Aldrich 99.6%) and NaF (Analit.Analytic grade) following the method of Rodríguez-Reyna *et al.* (2006) and Fuentes *et al.* (2006). Once the mechanochemical processing finished, the sample was heated in a tube furnace for 15 h at 1073 K in air atmosphere. Conventional X-ray powder diffraction data showed reflections that match with the isostructural oxyapatite $\text{NaY}_9(\text{SiO}_4)_6\text{O}_2$ (PDF file 35–404). At this step of synthesis, the sample exhibited very poor crystallinity. After an additional thermal treatment at 1123 K, the crystallization of the sample was reached with the presence of quartz (PDF file 46–1045) as a secondary phase. From wavelength dispersive spectrometry (WDS), chemical analysis was performed by means of a Jeol JXA-8900R, EPMA spectrometer.

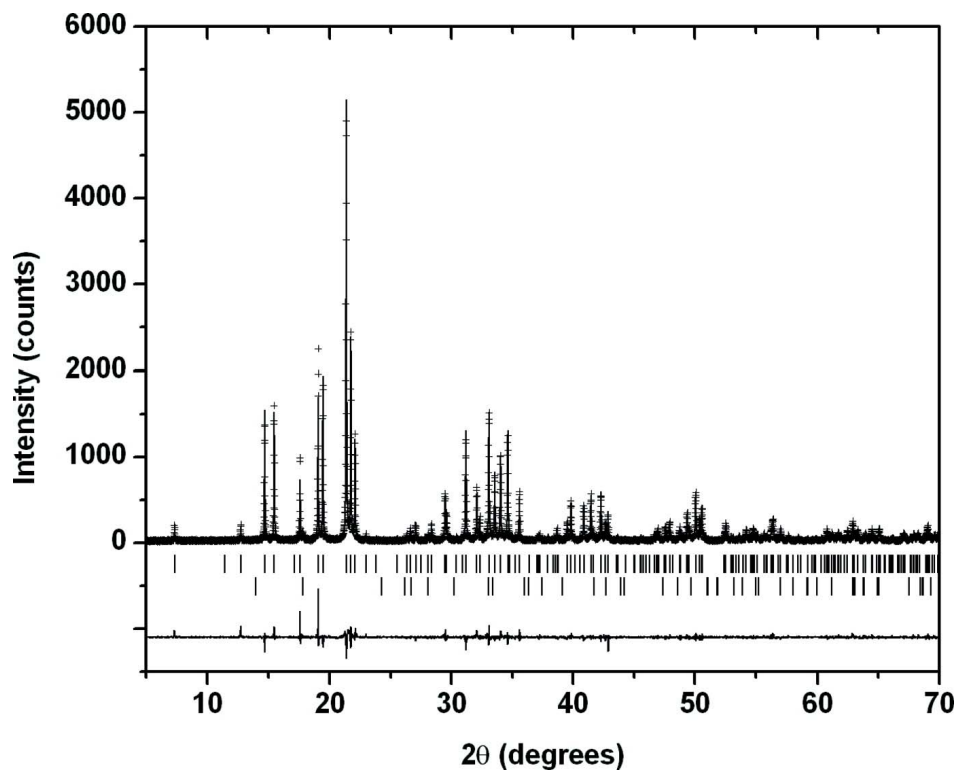
The average atomic content with standard uncertainty for each element in the sample were 12.4(1.9) for sodium, 42.2(4.6) for holmium and 45.2(6.3) for silicon, and give a Na:Ho ratio of 0.29. The expected values, according to the initial mixture of reactivities were 12.5 for sodium, 50.0 for holmium and 37.5 for silicon. These quantities changed as consequence of the process of mechanical milling. Fluorine could not be observed so the phase originally labeled as OAp could be considered as pure oxyapatite phase. The atomic content for each element in the unit cell for OAp was calculated dividing by 5.46 the averaged WDS values giving 2.27 for sodium, 7.23 for holmium and 8.28 for silicon. The excess of silicon was interpreted taking into account the presence of quartz measured as a secondary phase by x -ray diffraction. Therefore, the content of silicon had to be split in such way that 6 silicon atoms were corresponded to OAp

and 2.28 to quartz for each unit cell of oxyapatite.

S3. Refinement

The incident beam was calibrated using LaB₆ (*NIST* SRM 660) as reference standard. The starting parameters for performing the Rietveld refinement were, for the OAp phase, the data from the isostructural NaY₉(SiO₄)₆O₂ (ICSD 27191, Gunawardane *et al.*, 1982); and for quartz the data from ICSD 90145 (Gualtieri, 2000). Atomic coordinates were refined for the OAp phase considering the holmium and sodium atoms distributed in each one of the two available sites according to the Na:Ho ratio of 0.29 (obtained by WDS). In the following step, the occupation factors for Na and Ho were constrained in such a way that the total amount of both Na and Ho be constant keeping the Na:Ho ratio at 0.29. This ratio was allowed to change for each one of the crystallographic sites. At the end of the refinement, the thermal isotropic parameters were refined independently for each site. These parameters were set to the same refined value for all the O atoms in the structure.

Bond valence calculations were made using the recommended bond-valence parameters for oxides published by Brese & O'Keeffe (1991). Bond valence sum around Ho1 and Ho2 gave the values of 3.01 and 2.75 respectively, being the last lower than the expecting valence of 3. One way to explain the low bond valence sum is considering the Na substituting for Ho. In such case, bond valence sum for Na2 in the Ho2 site is found to be 1.51, and the weighted bond valence sum results equal to the weighted atomic valence when the fraction of Na2 is 0.33 in the Ho2 site. This quantity is reasonably close to 0.38 obtained by Rietveld refinement. For the Ho1 site, the bond valence sum around Ho is practically the expecting valence of 3 which agrees with the very low proportion of Na (0.12) obtained in the refinement. For the Ho1—O4 bonds there are three Ho1 atoms coordinated to O4 oxygen with a bondlengths of 2.197 Å. Each Ho1—O4 bond contributes with a bond valence of 0.62 giving a bond valence sum of 1.87. This value agrees with the fact that this site is partially occupied by oxygen O4 by an occupation factor of 0.36. With all this results, the chemical formula obtained was found to be Na_{2.27}Ho_{7.73}(SiO₄)₆O_{0.72}, which is charge balanced. The composition agrees with the WDS results and sodium content. The final Rietveld refinement of the synchrotron diffraction pattern is shown in Fig. 1 and the crystal structure is represented in Fig. 2.

**Figure 1**

Rietveld refinement for OAp employing synchrotron radiation data. Observed (crosses), calculated (solid line) and difference (bottom trace) plots are represented. Vertical marks correspond to the allowed Bragg reflections for OAp (first row) and SiO₂ (second row).

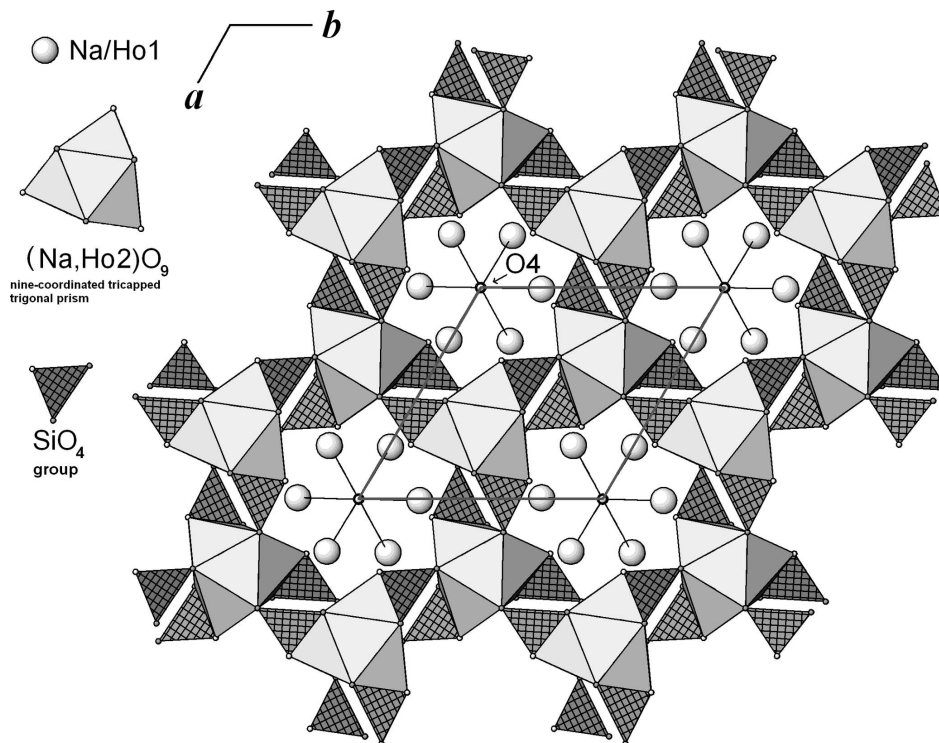
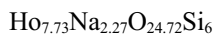


Figure 2

Structural representation of $\text{Na}_{2.27}\text{Ho}_{7.73}(\text{SiO}_4)_6\text{O}_{0.72}$.

Sodium holmium orthosilicate oxyapatite

Crystal data



$M_r = 1891.09$

Hexagonal, $P6_3/m$

Hall symbol: -P 6c

$a = 9.3405 (1) \text{ \AA}$

$c = 6.7638 (1) \text{ \AA}$

$V = 511.05 (1) \text{ \AA}^3$

$Z = 1$

$F(000) = 822.8$

$D_x = 6.145 \text{ Mg m}^{-3}$

Synchrotron radiation, $\lambda = 1.033490 \text{ \AA}$

$T = 295 \text{ K}$

white

flat sheet, $15 \times 15 \text{ mm}$

Specimen preparation: Prepared at 1123 K

Data collection

SSRL
diffractometer

Radiation source: synchrotron source

Si(111) monochromator

Specimen mounting: packed powder sample
container

Data collection mode: reflection

Scan method: step

$2\theta_{\min} = 5.0^\circ$, $2\theta_{\max} = 70.0^\circ$, $2\theta_{\text{step}} = 0.01^\circ$

Refinement

Least-squares matrix: full with fixed elements
per cycle

$R_p = 0.10$

$R_{\text{wp}} = 0.14$

$R_{\text{exp}} = 0.11$

$R_{\text{Bragg}} = 0.04$

$R(F^2) = 0.03$

$\chi^2 = 1.613$

6501 data points

Excluded region(s): none

Profile function: conventional pseudo-Voigt

22 parameters

0 restraints

Weighting scheme based on measured s.u.'s

$(\Delta/\sigma)_{\max} = 0.05$

Background function: linear interpolation
 between a set of background points with
 refinable heights
 Preferred orientation correction: none

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Ho1	0.2373 (2)	0.0042 (3)	0.25	0.0014 (4)	0.875 (2)
Na1	0.2373 (2)	0.0042 (3)	0.25	0.0014 (4)	0.125 (2)
Ho2	0.3333	0.6666	-0.0028 (9)	0.0013 (8)	0.620 (2)
Na2	0.3333	0.6666	-0.0028 (9)	0.0013 (8)	0.380 (2)
Si	0.368 (1)	0.397 (1)	0.25	0.014 (3)	
O1	0.246 (1)	0.334 (1)	0.444 (2)	0.030 (4)	
O2	0.490 (2)	0.312 (2)	0.25	0.030 (4)	
O3	0.523 (2)	0.403 (2)	0.75	0.030 (4)	
O4	0.0	0.0	0.25	0.030 (4)	0.358

Geometric parameters (\AA , $^\circ$)

Ho1—O1 ⁱ	2.42 (1)	Ho2—O2 ^{viii}	2.29 (1)
Ho1—O1 ⁱⁱ	2.24 (1)	Ho2—O2 ^{ix}	2.29 (1)
Ho1—O1 ⁱⁱⁱ	2.42 (1)	Ho2—O2 ^x	2.29 (2)
Ho1—O1 ^{iv}	2.24 (1)	Ho2—O3 ^{viii}	2.45 (1)
Ho1—O2	2.66 (1)	Ho2—O3 ^{ix}	2.45 (2)
Ho1—O3 ⁱⁱ	2.35 (2)	Ho2—O3 ^x	2.45 (1)
Ho1—O4	2.197 (2)	Si—O1	1.64 (1)
Ho2—O1 ^v	2.82 (2)	Si—O1 ^{vi}	1.64 (1)
Ho2—O1 ^{vi}	2.82 (1)	Si—O2	1.68 (3)
Ho2—O1 ^{vii}	2.82 (1)	Si—O3 ^{ix}	1.62 (2)
O1 ^v —Ho2—O3 ^{viii}	60.3 (7)		

Symmetry codes: (i) $-x+y, -x, z$; (ii) $y, -x+y, z-1/2$; (iii) $-x+y, -x, -z+1/2$; (iv) $y, -x+y, -z+1$; (v) $-x+y, -x+1, -z+1/2$; (vi) $x, y, -z+1/2$; (vii) $-y+1, x-y+1, -z+1/2$; (viii) $x-y, x, z-1/2$; (ix) $-x+1, -y+1, z-1/2$; (x) $y, -x+y+1, z-1/2$.