

Structural Characterization of $\text{Na}_{0.96}\text{Ho}_{9.04}(\text{SiO}_4)_6\text{Cl}_{0.02}\text{O}_{1.98}$ Apatite Prepared by Mechanical Milling

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Abstract In this paper we report the synthesis and structural characterization of $\text{Na}_{0.96}\text{Ho}_{9.04}(\text{SiO}_4)_6\text{Cl}_{0.02}\text{O}_{1.98}$ apatite prepared by mechanical milling at room temperature, in which well crystallized sample was obtained after heating the sample at 1123 K. The crystal structure study was carried out by synchrotron radiation diffraction. This apatite crystallizes in the hexagonal space group $P6_3/m$ (No. 176) with cell parameters $a = 9.3444(1) \text{ \AA}$, $c = 6.7611(1) \text{ \AA}$, unit cell volume of $511.27(1) \text{ \AA}^3$ and $Z = 1$. As in other rare-earth orthosilicate apatites, it was found that sodium cations are mixed with holmium occupying the $4f$ position at the center of tricapped trigonal prisms; while holmium fully occupies the $6h$ position at the center of a seven-coordinated polyhedron. No vacancies are present in the two crystallographic sites available for holmium atoms. The chemical composition was established by wavelength dispersive spectroscopy.

Keywords Synchrotron radiation · Oxychloroapatite · Mechanochemical synthesis · WDS microanalysis

Introduction

Apatites with general formula $\text{M}_{10}(\text{XO}_4)_6\text{Z}_2$ are labile to 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+} (in some cases Si^{4+} , Ge^{4+} or V^{4+}). Most apatites crystallize in the hexagonal system with symmetry given by the space group $P6_3/m$ (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 $\text{M}'_x\text{M}''_{10-x}$ $(\text{SiO}_4)_6\text{O}_{3-x}$ oxyapatites, as in $\text{NaNd}_9(\text{GeO}_4)_6\text{O}_2$ [1] and $\text{LiY}_9(\text{SiO}_4)_6\text{O}_2$ [2]. Other apatites with M being a trivalent cation are the oxyapatites $\text{Nd}_{9.33}\square_{0.77}(\text{SiO}_4)_6\text{O}_2$ and $\text{La}_{9.33}\square_{0.77}(\text{SiO}_4)_6\text{O}_2$ with interesting physical properties as oxide ionic conductors [3, 4]. In the last formulas, the cation vacancy has been represented by the symbol \square . Three-dimensional framework of hexagonal oxyapatites in which mobile O^{2-} ions in the channel along the c -axis give rise to a solid state electrolyte, have potential oxide ionic conductivity, and is one of the basis for devices like fuel cells, sensors and oxygen pumps [5].

The aim of this work was to synthesize a sodium holmium silicate oxychloroapatite by mechanical milling [6, 7] in order to study carefully its crystal structure, crystal chemistry and crystallinity as well as the nature of the chemical substitutions in this kind of rare-earth oxyapatites. The technique of mechanical milling offers the advantage of obtain a high degree of homogeneity avoiding the necessity to apply a thermal treatment for obtaining this type of apatites [8, 9].

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Experimental

Synthesis of the Sample

Sodium holmium orthosilicate oxychloroapatite (OxClAp) was prepared considering the nominal composition $\text{Na}_2\text{Ho}_8(\text{SiO}_4)_6\text{Cl}_2$ from stoichiometric mixtures of Ho_2O_3 (Aldrich, 99.9%), SiO_2 (Aldrich, 99.6%) and NaCl (Merck, 99.5%). This mixture was first powdered using an agate mortar; and then was placed in an agate vial with agate balls in such a way that the weight ratio between the balls and the sample was 11:1. The mechanochemical synthesis was carried out milling in air for 16 h using a FRITSCH Pulverisette mill model 06.102, with a rotating speed of 612 rpm. Once the mechanochemical processing finished, the sample was heated in a tube furnace for 19 h at 1123 K in air atmosphere. The characterization of the sample by conventional X-ray powder diffraction data after the ball milling process showed reflections that could be explained on the basis of the isostructurality to oxyapatite phase $\text{NaY}_9(\text{SiO}_4)_6\text{O}_2$, PDF file 35-404, as shown in the above plot in the Fig. 1. At this step of synthesis, the sample

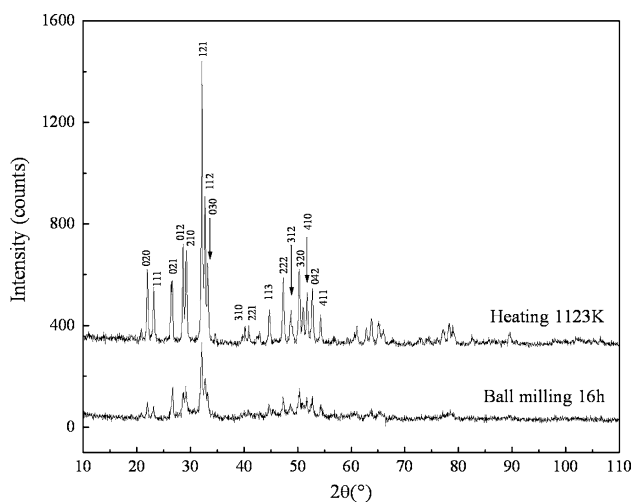


Fig. 1 Above: conventional X-ray powder diffractogram for the sample after 16 h of ball milling and heating at 1123 K in which the reflections was interpreted as belonging from an apatite phase isostructural to $\text{NaY}_9(\text{SiO}_4)_6\text{O}_2$ [10]. Bottom: diffractogram of the sample after mechanical milling

exhibits very poor crystallinity. After the thermal treatment at 1123 K, the crystallization was induced as can be seen in the upper powder diffractogram of Fig. 1. This diffractogram presents more definite reflections from the OxClAp phase than the diffractogram shown at bottom of Fig. 1, and shows also the presence of quartz (PDF file 46-1045) identified as a secondary phase.

Chemical Analysis

The data acquisition for chemical analysis by wavelength dispersive spectrometry (WDS) was performed in a JEOL JXA-8900R, EPMA spectrometer. For this technique, a droplet of resin was placed in a small hole of a plastic sample container. In the hole, the sample of interest was placed, and shine polished. At the end of the preparation, the sample container was cleaned with ethanol using an ultrasonic cleaner during 1 min. Obsidian with Cl and Na; $\text{HoP}_5\text{O}_{14}$ and quartz from 53 Minerals Standard-SPI # 02753-AB-Serial No. 02148 were used as reference standards for performing the quantification of atomic concentrations of the elements present in the nominal stoichiometry of the sample (Table 1). The correction method for depth and absorption of the beam was employed (ZAF).

Structural Characterization

The powder diffraction data of the sample phase was measured using the X-ray powder diffractometer located at beam line 2–1 of the Stanford Synchrotron Radiation Laboratory (SSRL) [10]. A Si (111)-based detector was used on the powder diffractometer which receives the incident radiation with 12 keV energy. The wavelength used was $1.03349 \pm 0.00007 \text{ \AA}$ which was obtained calibrating with the reference standard of LaB_6 (NIST SRM 660) over a full range of scattering angle 2θ from 5 to 70 degrees.

The structural model used for the apatite phase was established considering the isostructural compound $\text{NaY}_9(\text{SiO}_4)_6\text{O}_2$ reported by Gunawardane et al. [11] (ICSD 27191). For this compound, the chemical formula $\text{Na}_x\text{Y}_{10-x}(\text{SiO}_4)_6\text{O}_{2-y}\text{Cl}_y$ represents the way in which the

Table 1 Chemical composition (atomic percent) obtained by WDS analysis on six zones in the sample

%At	Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Average	Average/5.22	Assigned phase
Cl	0.08	0.00	0.270	0.10	0.12	0.18	0.12	0.022	Apatite
Na	10.50	10.93	9.05	9.16	8.42	10.91	9.83	1.883	
Ho	45.22	41.52	43.50	41.41	38.23	44.52	42.40	8.122	
Si	44.19	47.51	47.18	49.33	53.19	44.32	47.62	6.000	
								3.122	Quartz

sodium and chlorine ions are introduced in the apatite structure substituting the yttrium and oxygen ions, respectively. In the present work the nominal formula used for holmium chlorapatite, the possible incorporation of sodium and chlorine was represented as $\text{Na}_x\text{Ho}_{10-x}(\text{SiO}_4)_6\text{O}_{2-y}\text{Cl}_y$. Here, the sum of holmium and sodium is 10, and its ratio with silicon 1.67. The atomic content for each element in the unit cell can be reached if the average values listed in Table 1 (eighth column) are divided by 5.22. According to the X-ray diffraction data, quartz is a secondary phase contained in the sample and it is the explanation for an excess of silicon in Table 1, which content splits giving 6 silicon atoms for OxClAp and 3.122 for quartz in the ninth column of Table 1.

Taking into account the results discussed before, the chemical composition for the OxClAp phase was considered as $\text{Na}_{1.88}\text{Ho}_{8.012}(\text{SiO}_4)_6\text{Cl}_{0.02}\text{O}_{1.98}$, for the purpose of the Rietveld refinement. The charge balance is not zero in this chemical formula because of the lack of knowledge on the precise model for ionic substitution and the normal experimental deviations that can be measured from the WDS technique. This problem was carefully analyzed at the end of the refinement, as can be discussed later. Beside apatite and quartz, a small amount of a third phase identified as holmium hydroxide $\text{Ho}(\text{OH})_3$ (PDF file 83-2040) was identified only by synchrotron diffraction measurements: its stronger reflection 010 appears at 10.81° in 2θ . The starting parameters for the Rietveld refinement of these secondary phases were those reported by Gualtieri, ICSD 90145 for quartz [12], and by Beall et al., ICSD 200096 for holmium hydroxide [13].

The Rietveld refinement of the synchrotron diffraction data was made using the Fullprof program [14]. A pseudo-Voigt function modified by Thompson, Cox and Hastings [15] was chosen to generate the peak shape of the diffraction reflections. The following parameters were refined: zero point and scale factors, cell parameters, half-width and isotropic thermal coefficients for each one of the three phases. Atomic coordinates were only refined for the OxClAp phase. In this last case, after the refinement of atomic coordinates (keeping the starting values for occupation factors for Na and Ho) the thermal isotropic parameters were refined giving very high values. This situation changed when the occupation factors for Na and Ho were refined, and acceptable values for their thermal coefficients were reached. The final chemical composition for OxClAp phase was $\text{Na}_{0.96}\text{Ho}_{9.04}(\text{SiO}_4)_6\text{Cl}_{0.02}\text{O}_{1.98}$ with reasonable agreement with WDS results and acceptable charge balance of 0.1. The background was refined first by mean of a linear interpolation between 100 background points with adjustable heights. At the end of the refinement, the values for all of these heights of the background were fixed.

Conventional X-Ray Diffraction

X-ray powder diffraction data were collected at room temperature in a Bruker D8 Advance diffractometer with vertical goniometer, fixed diffracted secondary beam graphite monochromator and scintillation counter. A $\text{CuK}\alpha$ anode operating at 40 kV and 30 mA was used. In order to perform a structural analysis by the Rietveld method, the intensity counts were obtained using the step/scan mode with a step size of 0.02° and counting time of 10 s per step covering a 2θ range from 5 to 110 degrees. Lanthanum hexaboride, LaB_6 (NIST SRM 660) was used as reference standard.

The structural models used for the refinement were the same that those used for the synchrotron case except for holmium hydroxide which could not be detected in the conventional diffraction pattern. Two phases were then refined (OxClAp and quartz). A pseudo-Voigt function modified by Thompson, Cox and Hastings [15] was chosen to generate the peak shape of the diffraction reflections. The parameters refined in this case were: zero point and scale factors, cell parameters and half-width microstructural parameters and atomic coordinates for the OxClAp phase.

Results and Discussion

The final Rietveld refinement is shown in Fig. 2 and the crystal data and structure refinement parameters are summarized in Table 2. The atomic coordinates and isotropic thermal displacements for OxClAp appear in Table 3;

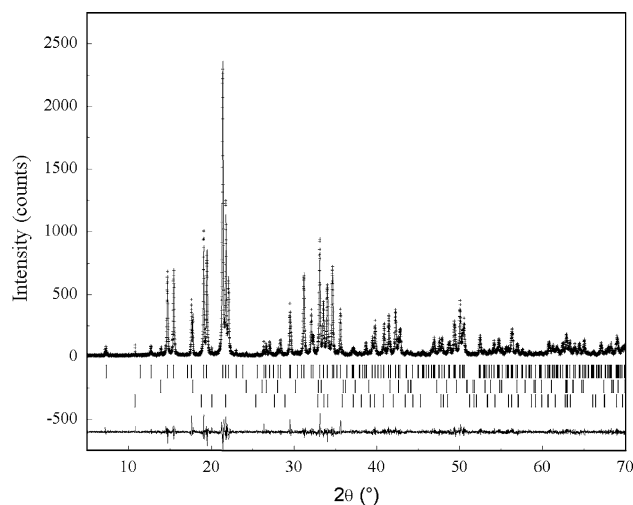


Fig. 2 Rietveld refinement for OxClAp employing synchrotron radiation data. Observed (*crosses*), calculated (*solid line*) and difference (*bottom trace*) plots are represented; *vertical marks* correspond to the allowed Bragg reflections for OxClAp (*top*), SiO_2 (*middle*) and $\text{Ho}(\text{OH})_3$ (*bottom*)

Table 2 Crystal data and structure refinement parameters for $\text{Na}_{0.96}\text{Ho}_{0.04}(\text{SiO}_4)_6\text{Cl}_{0.02}\text{O}_{1.98}$, and the secondary phases α -quartz and holmium hydroxide

Compound	$\text{Na}_{0.96}\text{Ho}_{0.04}(\text{SiO}_4)_6\text{Cl}_{0.02}\text{O}_{1.98}$	SiO_2	$\text{Ho}(\text{OH})_3$
Chemical formula	$\text{Cl}_{0.02}\text{Ho}_{0.04}\text{Na}_{0.96}\text{O}_{25.98}\text{Si}_6$	O_2Si	H_3HoO_3
Formula weight	2097.40	60.09	215.95
Crystal system	Hexagonal	Hexagonal	Hexagonal
Space group	$P 6_3/m$ (No. 176)	$P 3_22$ (No. 152)	$P 6_3/m$ (No. 176)
Unit cell dimensions (Å)	$a = 9.3444(1)$ $c = 6.7611(1)$	$a = 4.9252(3)$ $c = 5.410(1)$	$a = 6.323(1)$ $c = 3.527(3)$
$V(\text{Å}^3)$	511.27(2)	113.65(2)	122.04(11)
Z	1	3	2
Density (g/cm^3)	6.812	2.634	5.877
Independent reflections	293	81	83
Profile refined parameters	33	33	33
Reliability factors	$R_p = 0.10$, $R_{wp} = 0.14$, $R_{exp} = 0.11$, $\chi^2 = 1.21$	$R_p = 0.10$, $R_{wp} = 0.14$, $R_{exp} = 0.11$, $\chi^2 = 1.21$	$R_p = 0.10$, $R_{wp} = 0.14$, $R_{exp} = 0.11$, $\chi^2 = 1.21$
Structure factor	$R_B = 0.03$, $R_F = 0.03$	$R_B = 0.10$, $R_F = 0.08$	$R_B = 0.28$, $R_F = 0.08$

Table 3 Atomic coordinates and isotropic thermal displacements for $\text{Na}_{0.96}\text{Ho}_{0.04}(\text{SiO}_4)_6\text{Cl}_{0.02}\text{O}_{1.98}$

	Site	x	y	z	$U_{iso}(\text{Å}^2)$
Ho(1)	6h	0.2370(2)	0.0028(4)	$\frac{1}{4}$	0.0005(2)
Na, Ho(2)	4f	$\frac{1}{3}$	$\frac{2}{3}$	$-0.0008(7)$	0.0005(2)
Si	6h	0.3742(10)	0.4000(10)	$\frac{1}{4}$	0.0018(2)
O(1)	12i	0.2465(11)	0.3350(11)	0.4381(14)	0.008(3)
O(2)	6h	0.4851(18)	0.3202(20)	$\frac{1}{4}$	0.008(3)
O(3)	6h	0.5189(19)	0.3947(20)	$\frac{3}{4}$	0.008(3)
O(4)	2a	0	0	$\frac{1}{4}$	0.008(3)
Cl	2a	0	0	$\frac{1}{4}$	0.008(3)

while the crystal structure is represented in Fig. 3 and its main interatomic distances and angles are listed in Table 4.

The atomic arrangement of OxClAp belongs to the fluorapatite structural type. One feature of this structure is the triangular coordination for fluorine, which in OxClAp is replaced by both O(4) and Cl occupying the 2a Wyckoff position. At the vertexes of this coordination-triangle there are three Ho(1) atoms occupying the 6h position with a Ho(1)–Ho(1) distance of 3.812(5) Å. In turn, each Ho(1) is coordinated with O(4)/Cl and other six oxygen atoms forming a distorted pentagonal bipyramid. The possibility of substitution for Ho(1) by Na was carefully considered as follows: since the Ho(1)–Ho(1) distance is 3.812(5) Å and it represents the long of the coordination-triangle for O(4)/Cl, the corresponding distance from a vertex to the triangle centre is 2.2 Å, which is approximately the sum of ionic radii for oxygen (1.36 Å) and holmium (0.96 Å), so the

possibility that Ho(1) could be replaced by sodium (ionic radius of 1.24 Å) was discarded because of its higher size and only could have been explained if a larger distance for Ho(1)–Ho(1) had been obtained from the experimental data of table 4. The other independent position for Ho atoms, labeled as Ho(2), is at Wyckoff position 4f, coordinated with nine oxygens forming a tricapped trigonal prism. At this position, the sodium atoms are present (Table 3) with an occupation factor of 0.24, while for holmium it is 0.76. The trigonal prisms are piled up connected one to another sharing their bases forming a column along the c -axis. The bases of the tricapped trigonal prisms are triangles that alternatively are composed by O(2) and O(3) along the c -axis; being the capped oxygens of the polyhedra the O(1) oxygens. Silicon tetrahedron presents a C_{1h} point symmetry at Wyckoff position 6h and two of its oxygens, O(2) and O(3), interconnecting the bases of two adjacent columns of trigonal tricapped prisms. The other two vertexes of the SiO_4 tetrahedron are the O(1) capped oxygens of the trigonal tricapped prisms.

Summary and Conclusion

The crystal structure of OxClAp has an arrangement similar to some other alkaline rare-earth oxyapatites already reported such as $\text{NaY}_9(\text{SiO}_4)_6\text{O}_2$ [11] and $\text{LiY}_9(\text{SiO}_4)_6\text{O}_2$ [2], where the alkaline metal shares the nine-coordinated site with a rare-earth cation. The incorporation of alkaline metal in this site is achieved by the substitution of O(4) by a monovalent anion in order to maintain the charge

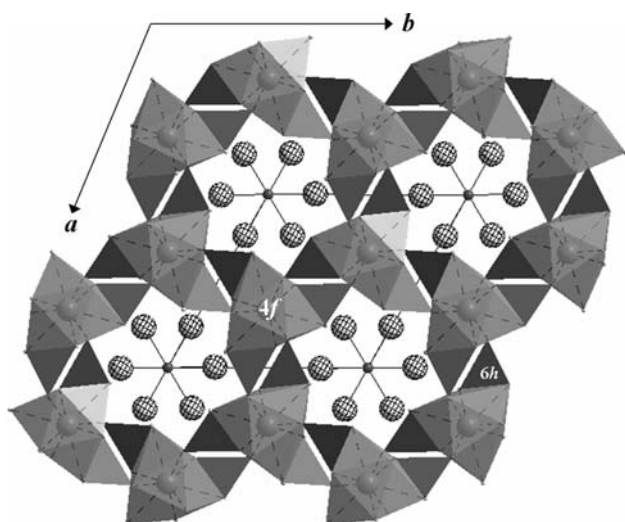


Fig. 3 Structural representation of $\text{Na}_{0.96}\text{Ho}_{9.04}(\text{SiO}_4)_6\text{Cl}_{0.02}\text{O}_{1.98}$ along the c axis. The tricapped trigonal prisms are represented in light gray color, while the $[\text{SiO}_4]^{4-}$ groups appear as dark gray tetrahedra. The squared-hachured spheres represent holmium atoms in the $6h$ Wyckoff positions

Table 4 Relevant bond distances (Å) and angles (°) for $\text{Na}_{0.96}\text{Ho}_{9.04}(\text{SiO}_4)_6\text{Cl}_{0.02}\text{O}_{1.98}$

Ho(1)–O(1)	2.395(9) 2×
Ho(1)–O(1)	2.279(9) 2×
Ho(1)–O(2)	2.701(14)
Ho(1)–O(3)	2.31(2)
Ho(1)–O(4)	2.201(3)
Ho(1)–Ho(1)	3.812(5)
Na, Ho(2)–O(1)	2.816(12) 3×
Na, Ho(2)–O(2)	2.350(15) 3×
Na, Ho(2)–O(3)	2.431(16) 3×
Si–O(1)	1.639(11) 2×
Si–O(2)	1.55(2)
Si–O(3)	1.659(18)
O(1)–Si–O(3)	109.5(11) 2×
O(1)–Si–O(2)	111.1(16) 2×
O(1)–Si–O(1)	101.8(9)
O(2)–Si–O(3)	113(2)

balance. Such is the case of chlorine in OxClAp. According to the X-ray powder diffraction measurements this compound is possible to obtain simply by mechanical milling.

The supplementary material has been sent to the Fachinformationzentrum Karlsruhe, Abt. PROKA, 76344 Eggenstein-Leopoldshafen, Germany, as supplementary material with CSD-number 419686 and can be obtained by contacting the FIZ (quoting the article details and the corresponding CSD number).

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