Article

Interaction Between FeOOH and NaCl at Extreme Conditions: Synthesis of Novel $\text{Na}_2\text{FeCl}_4\text{OH}_x$ Compound

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Received: 25 November 2019; Accepted: 30 December 2019; Published: 5 January 2020

Abstract: Iron(III) oxide-hydroxide, FeOOH, is abundant in the banded iron formations (BIFs). Recent studies indicate that BIFs may carry water down to the lower mantle with subducting slabs. The previous experiments investigating the properties of FeOOH at extreme pressures (P) and temperatures (T) were performed in diamond anvil cells (DACs), where it was compressed inside alkali metal halide pressure-transmitting media (2). Alkali metal halides such as NaCl or KCl are expected to be chemically inert; therefore, they are widely used in DAC experiments. Here, we report the chemical interaction between FeOOH and NaCl pressure medium at 107(2) GPa and 2400(200) K. By means of single-crystal X-ray diffraction (SC-XRD) analysis applied to a multigrain sample, we demonstrate the formation of a $\text{Na}_2\text{FeCl}_4\text{OH}_x$ phase and provide its structural solution and refinement. Our results demonstrate that at high P - T conditions, the alkali metal halides could interact with hydrous phases and thus cannot be used as a pressure transmitting and thermal insulating medium in DAC experiments dedicated to studies of hydroxyl or water-bearing materials at high P - T .

Keywords: FeOOH; NaCl; extreme conditions; SC-XRD; DAC

1. Introduction

Hydrous phases have been attracting great interest in the geological community due to their importance for the behavior and physical properties of the Earth's mantle [1,2]. One of such compounds, α -FeOOH (stabilized as goethite at the ambient conditions, which is a common material in the banded iron formations, or BIFs), is expected to submerge into the lower mantle with subducting slabs, bringing water to the lowermost mantle and the core–mantle boundary (CMB), as it was suggested in some publications [3,4]. Recently, a number of studies were dedicated to studying the behavior of FeOOH at high P - T conditions, which show that FeOOH undergoes a series of phase transitions. A “pyrite-type” FeO_2H_x phase is expected to be stable at the P - T conditions of lowermost part of a mantle and core–mantle boundary [5–7]. This phase is attracting the attention of the community and is being intensively investigated via density functional theory calculations and spectroscopic studies [5–9]. In some experiments performed in DACs, alkali halides (such as KCl, for example, ref. [9]) are used as a pressure-transmitting medium and thermal insulator for laser heating. It is assumed that alkali halides are fully chemically inert and cannot complicate data analysis. However, at very high pressures and temperatures, the chemistry of materials may change, and iron oxyhydroxide could potentially interact with the alkali halides. Information on the possible reactions between FeOOH and alkali metal halides

at extreme conditions and the crystal structures of possible products is absent. Methodologically, it is of great importance to verify the reactivity between these species.

2. Materials and Methods

A FeOOH sample (Alfa Aesar, CAS: 20344-49-4) with a lateral diameter of $\sim 10\ \mu\text{m}$ and thickness of $\sim 5\ \mu\text{m}$ was loaded inside a sample chamber of a BX90-type diamond anvil cell (DAC) [10] equipped with two beveled Boehler-Almax type diamonds (culet diameter $80\ \mu\text{m}$). The sample chamber was made by pre-indenting Re oil-free gasket (initial thickness $200\ \mu\text{m}$, thickness after indentation $\sim 15\ \mu\text{m}$) and drilling a hole of $\sim 35\ \mu\text{m}$ diameter in it. A NaCl powder was used as both a pressure-transmitting medium and a reactant to check its possible interaction with FeOOH. The DAC was compressed to the desired pressure (the pressure was determined using the equation of state (EoS) of B2-structured NaCl [11]) and laser-heated at BL-10XU at SPring-8 (Sayo, Hyogo, Japan) [12]. The analysis of the reaction products was performed on the *T*-quenched sample at P2.02 DESY beamline [13] employing the single-crystal X-ray diffraction technique for laser-heated DACs as developed at Bayreuth University [14]. In order to locate the grain of a reaction product and collect the single-crystal X-ray diffraction (SC-XRD) dataset from it, the XRD mapping was performed by scanning the sample in vertical and horizontal directions with steps of three micrometers. After localizing grain(s) of interest, the step scans were recorded on a Perkin Elmer detector (XRD1621, Waltham, MA, USA) (sets of individual photographs (with equal exposure time, from 1 to 10 s) taken each 0.5° of DAC rotation in a range of $\pm 36^\circ$ around the ω axis of the goniometer).

Analysis of collected diffraction images was performed using *CrysAlis PRO* software (Agilent Technologies, Version 1.171.37.35) [15]. The structures were solved using the dual-space method and refined in the isotropic approximation by full-matrix least-squares refinements using SHELX software package (SHELX-2019, Universität Göttingen, Göttingen, Germany) software [16,17]. Crystal structure visualization made with the VESTA (Version 3.4.4) software [18].

3. Results

The compression of FeOOH in NaCl at ambient temperature to 107(2) GPa did not result in any chemical reaction. At this pressure, after double-side laser heating of the sample at $\sim 2400(200)\ \text{K}$, new sets of reflections on the XRD patterns of the *T*-quenched sample were observed. Consideration of powder and single-crystal diffraction data collected from the laser-heated sample suggests that several different phases are formed in the DAC (Figure S1). From the powder-diffraction data (Figure 1, Figure S1), we identified a cubic FeO_2H_x phase with a unit cell parameter $4.403(3)\ \text{\AA}$, which is in agreement with a recent literature reports [3,4], as well as a signal from a cubic B2-type NaCl ($a = 2.911(2)\ \text{\AA}$) and *hcp*-structured Re ($a = 2.6697(8)\ \text{\AA}$, $c = 3.923(2)\ \text{\AA}$) from the gasket. Remaining peaks on the powder XRD pattern belong to an unknown phase. Through the further analysis of the single-crystal data of decent quality obtained for several grains, we were able to index reflections belonging to two different co-existing orthorhombic phases. For the first phase, we found unit cell parameters $a = 2.5467(5)\ \text{\AA}$, $b = 9.640(2)\ \text{\AA}$, and $c = 11.580(2)\ \text{\AA}$, and a suggested space group $I_{mmm}2$ (#44) (further denoted as “ol-phase”) as determined by analysis of the 298 unique reflections and systematic absences. Unfortunately, the intensity of the Bragg reflections of this phase is too low, and the structure solution is not possible.

For the second new phase, analysis of single-crystal data allows determining the orthorhombic unit cell with parameters $a = 8.725(2)\ \text{\AA}$, $b = 6.180(3)\ \text{\AA}$, $c = 3.0679(12)\ \text{\AA}$. Further integration of a dataset allowed extracting the intensities of 315 Bragg reflections, which belong to the single grain, and a space group P_{bam} (#55) was determined (Figure S2). The quality of the data (Table 1) allowed performing structure solution and refinement. We found that this phase with a chemical formula $\text{Na}_2\text{FeCl}_4\text{OH}_x$ is the product of the chemical reaction between FeOOH and NaCl. Its crystal structure is shown in Figure 2 (crystal data, information on the data collection and structure refinement details summarized in Tables 1 and 2). We refined atomic displacement parameters in isotropic approximation due to the limited quality of the data collected in the DAC at pressure over megabar. Due to the same reason,

positions of hydrogen atoms cannot be freely refined, and we fixed H-atoms at Wyckoff 8i position with a 1 Å distance to the oxygen atoms and site occupancy fixed at 0.25.

Figure 1. Le-Bail fitting of an XRD pattern of a mixture of NaCl and FeOOH at 107(2) GPa after laser-heating to 2400(200) K. Black line—convoluted experimental data from a Perkin-Elmer detector (diamond reflections masked), red line—calculated XRD signal from several phases. Color ticks below the diffraction curve represent the reflections of the phases described in a legend. $R_p = 12.49\%$.

Table 1. Crystallographic information on the $\text{Na}_2\text{FeCl}_4\text{OH}_x$.

Crystal Data	
Chemical formula	$\text{Na}_2\text{FeCl}_4\text{OH}_x$
M_r (g/mol)	260.6
Crystal system, space group	Orthorhombic, Pbam (#55)
Temperature (K), Pressure (GPa)	293, 107(2)
a, b, c (Å)	8.725 (2), 6.180 (3), 3.0679 (12)
V (Å ³)	165.41 (11)
Z	2
Radiation type	Synchrotron, $\lambda = 0.2892$ Å
μ (mm ^{−1})	0.61
Crystal shape	Cube
Crystal size (mm)	$0.01 \times 0.01 \times 0.01$
Data collection	
Diffractometer	P02.2, DESY
Absorption correction	Multi-scan (ABSPACK, [15])
$T_{\min}, T_{\max}$	0.538, 1
No. of measured, independent and observed [$I > 3\sigma(I)$] reflections	894, 432, 315
R_{int}	0.038
θ values (°)	$\theta = 3.2\text{--}18.4$
$(\sin \theta/\lambda)_{\text{max}}$ (Å ^{−1})	1.089
Range of h, k, l	$h = -16 \rightarrow 13, k = -8 \rightarrow 10, l = -5 \rightarrow 4$
Refinement	

Table 1. Cont.

Crystal Data	
R[F2 > 2σ(F2)], wR(F2), S	0.070, 0.071, 2.93
No. of reflections	315
No. of parameters	27
Δρ _{max} , Δρ _{min} (eÅ ^{−3})	2.07, −1.63

Software: CrysAlis PRO [15], SHELXT [16], SHELXL2014 [17].

Figure 2. The crystal structure of $\text{Na}_2\text{FeCl}_4\text{OH}_x$ at 107(2) GPa. (a) Polyhedral structural model. Yellow spheres—Na atoms, brown spheres—Fe atoms, Cl and O atoms shown as green and red spheres, correspondingly. Yellow and brown polyhedra represent the coordination of Na and Fe ions. White spheres show the possible (partially occupied) positions of H atoms. Dashed black lines—unit cell boundaries. (b) Fe coordination polyhedra with bond lengths. (c) Na coordination polyhedra with bond lengths.

Table 2. Atomic coordinates in the $\text{Na}_2\text{FeCl}_4\text{OH}_x$ structure.

Atom Number	Atom Name	Atomic Coordinates (x, y, z)	Occupancy	Isotropic Atomic Displacement Parameter (U , Å ²)	Wyckoff
1	Fe1	0.5, 0.0, 0.0	1	0.01	2 c
2	Cl1	0.2076, 0.3455, 0.0	1	0.012	4 g
3	Cl2	0.4251, 0.1907, 0.5	1	0.011	4 h
4	Na1	0.1645, 0.0701, 0.5	1	0.012	4 h
5	O1	0.0, 0.0, 0.0	1	0.002	2 a
6	H1	0.00380, 0.11683, 0.17495	0.25	0.0	8 i

In the orthorhombic $\text{Na}_2\text{FeCl}_4\text{OH}_x$ compound, the iron atoms coordinated with two crystallographically distinct chlorine (Cl1 and Cl2) atoms, forming just a slightly distorted octahedra (distortion index = 0.00125) with an average bond length of 2.044 Å. These FeCl_6 octahedra are stacked into the columns along the c direction, sharing the edges (Figure 2). The Na atoms are coordinated with seven chlorine atoms and two oxygen atoms, forming a monocapped antiprismatic polyhedron (Figure 2). Two oxygen and two chlorine atoms form a parallelogram base of antiprism (with an O1–Cl2–O1 angle of $74.42(8)^\circ$). These polyhedra are connected to each other through a common triangular and parallelogram faces and share the common edges with FeCl_6 octahedra (Figure 2). The coordination of Na in $\text{Na}_2\text{FeCl}_4\text{OH}_x$ is unusual for the Na and resembles the one described for La in LaOCl oxyhalides [19].

4. Discussion

While the stoichiometry of heavier atoms in the $\text{Na}_2\text{FeCl}_4\text{OH}_x$ compound is uniquely defined by structural refinement, the amount of hydrogen is not known. One could assign common (usual) oxidation states for Na, Cl, and O atoms (+1, −1, and −2, respectively), but for iron as a transition metal, several oxidation states are known to range from 0 to +4. The trivial charge balance considerations could not be easily implemented: the refinement of hydrogen atoms' positions and occupancies directly from the SC-XRD data is a complex task even at ambient conditions; for the experiments performed in the DACs, it is practically impossible in the most cases. Mössbauer or X-ray absorption near edge structure (XANES) spectroscopies could help to define the oxidation state of iron and therefore establish the amount of hydrogen in phase; however, in case of multiphase samples, the interpretation of spectroscopy data would be most probably ambiguous.

Another way would be to perform the crystallochemical analysis and compare the bond distances in $\text{Na}_2\text{FeCl}_4\text{OH}_x$ with Fe–Cl distances in other known compounds. Unfortunately, such a type of analysis is greatly complicated by very limited data on the high- P behavior of Fe,Cl-bearing compounds. By fitting the pressure–volume literature data on $\text{Fe}^{2+}\text{Cl}_2$ and Fe^{3+}ClO with the Birch–Murnaghan equation of state (EoS), we described the Fe–Cl bond evolution in FeCl_6 octahedra upon compression. Assuming that the structures of these compounds remain the same at high pressures, we compare extrapolated Fe–Cl bond lengths for $\text{Fe}^{2+}\text{Cl}_2$ and Fe^{3+}OCl and our experimental values at 107 GPa (Figure 3). The observed average Fe–Cl bond length in FeCl_6 octahedra in the $\text{Na}_2\text{FeCl}_4\text{OH}_x$ is 2.044 Å (see above). Extrapolated values for the Fe–Cl contact in FeOCl and FeCl_2 are ~2.6 Å and ~2.0 Å at 107 GPa.

While the coordination of iron in FeOCl is not the same as in $\text{Na}_2\text{FeCl}_4\text{OH}_x$ and the extrapolated Fe–Cl bond length is much higher, the iron in FeCl_2 is coordinated similarly, and the estimated Fe–Cl bonds of ~2 Å are very close to the observed Fe–Cl contact in our experiment. Therefore, one could suggest that iron in $\text{Na}_2\text{FeCl}_4\text{OH}_x$ is in the 2+ oxidation state, and therefore $x = 2$. Still, the iron oxidation state 3+ cannot be excluded: the reported values of Fe–Cl bond lengths for ferric iron in $\text{Fe}^{3+}\text{Cl}_6$ octahedra of FeCl_3 and $\text{K}_2\text{FeCl}_5(\text{H}_2\text{O})$ compounds are obviously much lower than those of ferrous iron chlorides at ambient conditions. Unfortunately, the lack of information on the compressibility of Fe^{3+} atoms octahedrally coordinated by Cl does not allow us to estimate the Fe–Cl distances at 107(2) GPa. Therefore, our crystallochemical considerations cannot confidently assign an oxidation state to the Fe atoms.

Figure 3. The estimation of a Fe–Cl bond length in different compounds at high pressures. FeCl_2 data are from [20], FeOCl data are from [21]. Experimental values of Fe–Cl bond length for FeCl_3 and $\text{K}_2\text{FeCl}_5(\text{H}_2\text{O})$ are from [22] and [23], correspondingly. Red star—experimental point for $\text{Na}_2\text{FeCl}_4\text{OH}_x$.

5. Conclusions

Our results demonstrate that at high P - T conditions, sodium halide reacts with FeOOH , forming a novel $\text{Na}_2\text{FeCl}_4\text{OH}_x$ compound. Thus, the alkali metal halides could interact with hydrous phases and thus cannot be used as a pressure-transmitting and thermal-insulating medium in DAC experiments dedicated to studies of hydroxyl or water-bearing materials at high pressure–high temperature conditions.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2075-163X/10/1/51/s1>, Figure S1: Representative X-ray diffraction pattern collected after laser-heating of FeOOH in NaCl at 2000(200) K and 107(2) GPa ($\lambda = 0.2892 \text{ \AA}$, P02.2 beamline at PETRAIII). (a) As collected 2D XRD image acquired with Perkin-Elmer detector during rotation of the DAC from -20° to $+20^\circ$ around the ω axis (“wide scan”). (b) Rolled up (‘cake’) representation of a selected 2D wide scan XRD pattern. Figure S2: Examples of reconstructed reciprocal planes for one of the domains of $\text{Na}_2\text{FeCl}_4\text{OH}_x$ phase at 107(2) GPa. (a), (b), and (c) panels show (hk-1), (h1l), and (2kl) planes correspondingly.

Author Contributions: Conceptualization, E.K. and L.D.; methodology, E.K., E.B., K.G., L.D., E.O. and L.Y.; investigation, E.K., L.Y., E.B., K.G., E.O., and L.D.; resources, E.O. and L.D.; data curation, E.K., L.Y., E.B., E.O., and L.D.; writing—original draft preparation, E.K. and L.D.; writing—review and editing, E.K., L.Y., E.B., K.G., E.O. and L.D.; funding acquisition, E.K., E.O., L.Y., and L.D. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Deutsche Forschungsgemeinschaft (DFG), grant number GRK 2156/1.

Acknowledgments: Authors thank the Deutsches Elektronen-Synchrotron for the provision of synchrotron beamtimes (P02.2). Authors are grateful for the SPring-8 for provision of synchrotron beamtime at BL10XU.

Conflicts of Interest: The authors declare no conflict of interest.

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