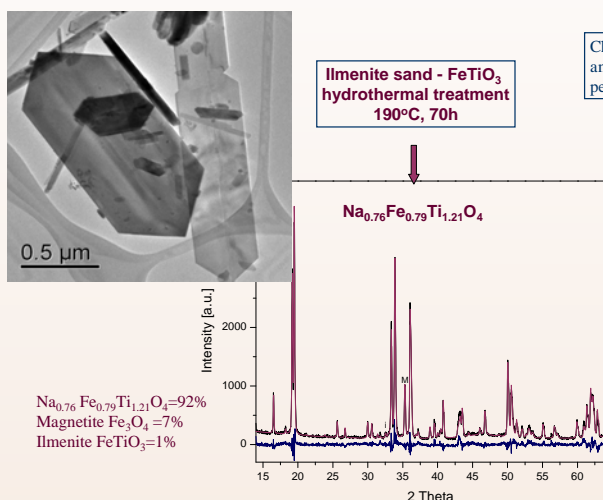Serbian Academy of Sciences and Arts

Na$_{0.76}$Fe$_{0.79}$Ti$_{1.21}$O$_4$ – the new CaFe$_2$O$_4$ structure type compound obtained from natural ilmenite sand under hydrothermal conditions

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CaFe$_2$O$_4$ structure type, named after the prototype compound, is a less known crystal structure from the A$_2$BX$_4$ stoichiometry. Its basic motif is a double rutile chain composed of octahedras connected by edges. A double chain itself is connected to another four double chains through corners, forming in that way tunnels oriented along the shortest unit-cell axis. In order to compensate the negative charge of framework, the tunnels are occupied most frequently by Na$^+$ or Ca^{2+} and more rarely by Sr^{2+} or Ba^{2+}. CaFe$_2$O$_4$ structure type compounds are generally obtained through a high-temperature synthesis route. Here, we report a simple low-temperature hydrothermal synthesis of Na$_x$Fe$_x$Ti$_{2-x}$O$_4$ phase with CaFe$_2$O$_4$ type structure, by reacting natural ilmenite sand (Millenium Inorg.Chem., Brazil) with 10M NaOH solution at temperatures bellow 200°C. The typical product is sodium-deficient Na$_x$Fe$_x$Ti$_{2-x}$O$_4$ phase obtained in content of 92wt%. Up to now there was just one report in literature on hydrothermal synthesis of a CaFe$_2$O$_4$ type compound related to Na$_3$Mn$_4$Te$_2$O$_{12}$ compound that adopts a superstructure intimately related to the CaFe$_2$O$_4$ structure type [1].

Ilmenite sand - FeTiO$_3$ hydrothermal treatment 190°C, 70h

Na$_{0.76}$Fe$_{0.79}$Ti$_{1.21}$O$_4$

Na$_{0.76}$Fe$_{0.79}$Ti$_{1.21}$O$_4$=92%
Magnetite Fe$_3$O$_4$ =7%
Ilmenite FeTiO$_3$=1%

Characterization of the products is done by X-ray powder diffraction followed by Rietveld refinement and quantitative phase analysis, in order to obtain crystal structure and to determine weight percentage of crystal phases present.
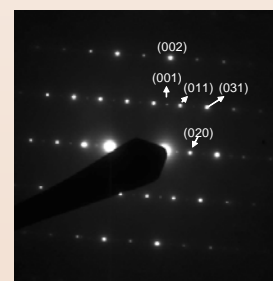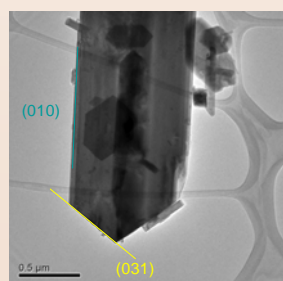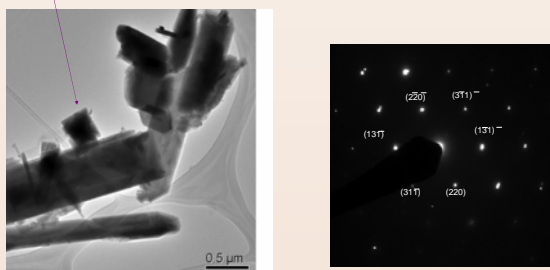
Table 1. Rietveld refinement data for Na$_{0.76}$Fe$_{0.79}$Ti$_{1.21}$O$_4$
Refined atomic positions and occupancy factors — **Crystal structure data**

Atom	Site	x	y	z	N$_j$
Na1	4c	0.24444(99)	0.34783(82)	0.75	0.76
B1 (Ti1)	4c	0.05986(35)	0.11390(35)	0.75	0.47
B1 (Fe1)	4c	0.05986(35)	0.11390(35)	0.75	0.53
B2 (Ti2)	4c	0.08608(37)	0.60468(31)	0.75	0.74
B2 (Fe2)	4c	0.08608(37)	0.60468(31)	0.75	0.26
O1	4c	0.31080(10)	0.64888(90)	0.75	1
O2	4c	0.39026(82)	0.99072(95)	0.75	1
O3	4c	0.46880(12)	0.21033(84)	0.75	1
O4	4c	0.05710(11)	0.92440(72)	0.75	1

Space group: Pnam (62)
Lattice parameters:
a=9.1230(4) Å
b=10.7469(4) Å
c=2.9562(1) Å

R$_B$=3.86%
R$_{wp}$=10.81%
S (goodness of fit) = 1.76

Magnetite Fe$_3$O$_4$ is the minority phase, which weight percentage is not higher than 7wt%. Residual un-reacted ilmenite can be remove by increasing synthesis time.

The as-prepared ferititanate is Na deficient with occupancy factor of 0.76. This corresponds well with the determined total content of Fe in the sites B1 and B2, estimated to be 0.79 (Table 1). This could mean that all trivalent cations in B1 & B2 sites, which are necessary for the charge compensation of the Na$_x$Fe$_x$Ti$_{2-x}$O$_4$ compound, are due to Fe^{3+}. The values of **x** defined by sodium-deficiency and Fe^{3+} content should be equal and therefore a small discrepancy obtained is probably within error range for conventional XRD technique. Another possible indication from N$_j$ for the Fe1 and Fe2 is that the Fe^{3+} might not be randomly distributed over these two sites, so far as conventional XRD can determine. This is also indicative from determined bond lengths: Ti1,Fe1-O is 1.95 Å, while Ti2,Fe2-O is 1.98 Å. Having in mind that the mean Ti-O bond length within octahedral polyhedron for many simple and complex oxides is around 1.96 Å, while the mean Fe-O distance assumed from the CaFe$_2$O$_4$ is 2.02 Å, obtained value of for Ti2,Fe2-O bond length is expected, while for Ti1,Fe1-O is somewhat smaller then it would be expected. Therefore, the indication of Fe3+ ordering still has to be verified by neutron diffraction.

TEM image of typical Na$_{0.76}$Fe$_{0.79}$Ti$_{1.21}$O$_4$ crystal and corresponding SEAD pattern

From the X-ray spectrum measured on a TEM, through Cliff-Lorimer ratio technique it was possible to calculate Ti/Fe ratio [2]:

$N_{Ti}/N_{Fe}=k_{TiFe}I_{Ti}/I_{Fe}$

to be 1.41 (estimating its relative error due to counting statistic of the peaks Ti-Kα and Fe-Kα, as lower than %).
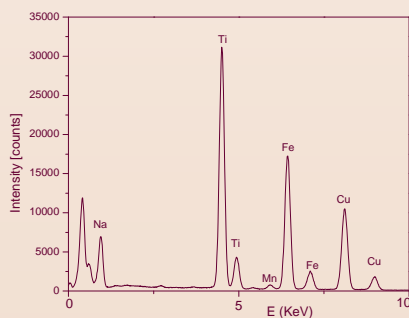

TEM image shows submicron to micron Na$_{0.76}$Fe$_{0.79}$Ti$_{1.21}$O$_4$ crystals with well defined crystal facets and growth direction. Zone axis is determined from SEAD pattern to be [100] while the direction of growth is [001] assuming Pnam space group. This means that the tunnels are oriented along the growth direction of the crystals. The crystals are thinnest in [100] direction. The crystallographic direction of [010] is perpendicular to the growth direction. The crystal facets are composed of {100}, {010} and {031} crystal planes, being {100} the most extended one.

This Ti/Fe ratio deviated ~ 8% from the one calculated from X-ray diffraction pattern (1.53), which suggests that the true Ti/Fe is most likely around 1.5, as indicated independently by two different approaches, Rietveld method and Cliff-Lorimer ratio technique.

Literature:
1. C.R. Feger and J.W. Kolis, Acta Cryst., C54 (1998) 1055.   2. Transmission Electron Microscopy IV, Spectrometry, D.B. Williams and C.B. Carter, Plenum Press NY, 1996, p. 600.

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