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Structure refinement of mixed oxides $\text{Fe}_x\text{Co}_{1-x}\text{Ta}_2\text{O}_6$

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Abstract

We report X-ray powder diffraction measurements performed on synthetic samples of the tapiolite-like $\text{Fe}_x\text{Co}_{1-x}\text{Ta}_2\text{O}_6$ solid solution. The crystal structure has been refined by the Rietveld method, by using the program FULLPROF. All the samples are tetragonal and were indexed to the space group $P4_2/mmm$. The end-members (FeTa_2O_6 and CoTa_2O_6) have unit-cell parameters quite similar to those previously published. The unit-cell parameters a and c for the mixed samples vary linearly with the cation substitution ($\text{Co} \rightarrow \text{Fe}$) according to the Vegard's law in all the range of substitution. © 2001 Elsevier Science Ltd. All rights reserved.

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The oxide FeTa_2O_6 [1–3], known as tapiolite, crystallises with the trirutile structure in space group $P4_2/mmm$, with Fe^{2+} and Ta^{5+} cations surrounded by O^{2-} octahedra, and successive Fe–O planes (at $z = 0$ and $z = 1/2$) separated by two Ta–O planes (at $z = 1/6$ and $z = 1/3$). The oxide CoTa_2O_6 [4] presents crystal structure isomorphous to FeTa_2O_6 , but a completely different magnetic structure. The FeTa_2O_6 magnetic structure consists of two families of antiferromagnetic (AF) planes. The uniaxial anisotropy of one family is rotated by 90° with respect to the other. The 3D magnetic lattice is a stacking of alternated planes from each family. The anisotropy field direction, on the basal plane, correlates with the symmetry of the local field originating from the oxygen belonging to the Fe atoms' coordination in the lattice. CoTa_2O_6 presents a very complex two-cone axis helical spin structure [4] with components on the basal plane as well as in the c -direction. Therefore, $\text{Fe}_x\text{Co}_{1-x}\text{Ta}_2\text{O}_6$ is a mixed oxide with competing anisotropy. Such systems lead to a tetracritical phase transition [5–7], whose experimental confirmation has been reported in several papers [8–13], from which we would like to highlight those referring to compounds isomorphous to K_2NiF_4 , the archetypal two-dimensional antiferromagnet [8,12].

As it is known [1,3,4,14], in the AB_2O_6 family the sublattice formed by the atoms A has the same symmetry as the Ni sublattice in K_2NiF_4 . This observation has motivated investigations to search for the existence of low-dimensional magnetic behaviour in these compounds. Indeed, this has been observed for compounds with $A = \text{Fe}, \text{Co}, \text{Ni}$ and Cr , and $B = \text{Ta}$ and Sb [1–4,14–17]. Now, extrapolating the similarities between K_2NiF_4 and AB_2O_6 systems to $\text{K}_2\text{Co}_x\text{Fe}_{1-x}\text{F}_4$ and $\text{Fe}_x\text{Co}_{1-x}\text{Ta}_2\text{O}_6$ systems, the latter one is expected to present competing anisotropic behaviour. To investigate this possibility we have prepared powder $\text{Fe}_x\text{Co}_{1-x}\text{Ta}_2\text{O}_6$ samples with $x = 0, 0.2, 0.5, 0.8$ and 1.0 , whose detailed crystal structure refinement is reported, for the first time, in the present paper. To substantiate the structural characterisation, we have performed some magnetic measurements. A detailed magnetic investigation is in progress.

As previously described [2], FeTa_2O_6 was prepared in vacuum, by the solid-state reaction of Fe , Fe_2O_3 and Ta_2O_5 . Appropriate amounts of the powdered reagents were mixed, ground, pelleted, encapsulated under vacuum ($p \cong 10^{-3}$ Pa) and heated at 1320 K for 48 h, with an intermediate regrinding after 24 h. After slow cooling, the sample was powdered to 320 mesh. CoTa_2O_6 was prepared in a similar way, but in air, instead of vacuum. As reported in a preliminary paper [18], for $\text{Fe}_x\text{Co}_{1-x}\text{Ta}_2\text{O}_6$ samples appropriate amounts of FeTa_2O_6 and CoTa_2O_6 were mixed and processed as for the FeTa_2O_6 preparation.

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Table 1

Cell-unit parameters obtained in the present work. All the samples were indexed to the space group $P4_2/mnm$. Numbers in parentheses designate $\pm 1\sigma$ on the last decimal given. The profile, R_p , and Bragg, R_B , agreement factors are given by

$$R_p = 100 \frac{\sum |y(\text{obs}) - y(\text{calc})|}{\sum y(\text{obs})} \quad R_B = 100 \frac{\sum |I(\text{obs}) - I(\text{calc})|}{\sum I(\text{obs})}$$

Sample	a (Å)	c (Å)	R_p (%)	R_B (%)
CoTa ₂ O ₆	4.7360(0)	9.174(1)	11.2	3.21
Fe _{0.2} Co _{0.8} Ta ₂ O ₆	4.7409(4)	9.178(0)	10.70	3.35
Fe _{0.5} Co _{0.5} Ta ₂ O ₆	4.7464(5)	9.186(1)	9.88	2.70
Fe _{0.8} Co _{0.2} Ta ₂ O ₆	4.7520(0)	9.193(1)	9.73	3.78
FeTa ₂ O ₆	4.7563(0)	9.198(7)	11.70	3.14

X-ray powder diffraction (XRD) patterns were obtained in Bragg–Brentano geometry by means of a Siemens diffractometer D500, equipped with a curved graphite monochromator and CuK α radiation (CuK $\alpha_1 = 1.5406$ Å, CuK $\alpha_2 = 1.5444$ Å) and calibrated with polycrystalline Si. Measurements were performed with a scan step of $0.02^\circ 2\theta$ in the 2θ range from 5 to 110° , with fixed counting time of 4 s. The program FULLPROF [19] was used for structure refinement.

The XRD patterns for all the samples were indexed to the space group $P4_2/mnm$, with unit-cell parameters as shown in Table 1. Our results for FeTa₂O₆ and CoTa₂O₆ are similar to those previously reported [1,4,15]. A typical pattern is displayed in Fig. 1, for the sample Fe_{0.5}Co_{0.5}Ta₂O₆. The refined structure of this sample is summarised in Tables 2 and 3. As for the other samples, there is no signal of spurious reflections and the refinement proceeded smoothly using the results for CoTa₂O₆ [4] as starting parameters. Besides the

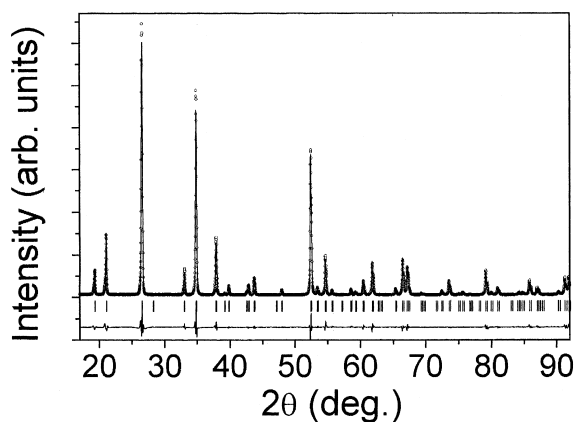


Fig. 1. Room-temperature X-ray powder diffraction patterns for Fe_{0.5}Co_{0.5}Ta₂O₆. The open circles represent observed data. The solid line represents the calculated pattern obtained with the Rietveld refinement. The line at the bottom is a plot of the residual spectrum, i.e. observed minus calculated intensities.

Table 2

Fractional atomic coordinates and isotropic thermal parameters for Fe_{0.5}Co_{0.5}Ta₂O₆ as obtained from Rietveld refinement. Numbers in parentheses designate $\pm 1\sigma$ on the last decimal given. $R_p = 9.88$ and $R_B = 2.70$

Atom	x	y	z	B (Å ²)
Fe	0	0	0	0.49(1)
Co	0	0	0	0.49(1)
Ta	0	0	0.33(1)	0.53(2)
O ₁	0.306(7)	0.306(7)	0	1.04(2)
O ₂	0.296(1)	0.296(1)	0.324(2)	1.04(2)

Table 3

Bond distances (Å) and angles (°) for Fe_{0.5}Co_{0.5}Ta₂O₆. Numbers in brackets designate $\pm 1\sigma$ on the last decimal given

(Fe,Co)–O1	2.05(1)	Ta–O1	2.02(7)
(Fe,Co)–O2	2.11(8)	Ta–O2	1.97(4)
		Ta–O2	1.98(8)
O1–(Fe,Co)–O1	180.000	O2–Ta–O2	176.273
O2–(Fe,Co)–O2	179.960	O1–Ta–O2	176.185
O2–(Fe,Co)–O2	99.512	O1–Ta–O2	96.084
O1–(Fe,Co)–O2	90.000	O1–Ta–O2	91.426
O2–(Fe,Co)–O2	80.488	O2–Ta–O2	88.657
		O2–Ta–O2	87.731
		O1–Ta–O1	80.101

visual inspection, the purity of the samples can be inferred from the low value of the agreement factors R_p and R_B . Thus, from XRD results it can be concluded that we have prepared well-crystallised single-phase samples.

Plots of the unit-cell parameters as a function of the iron concentration are presented in Fig. 2. As can be seen, the evolution of the cell parameters a and c obey the Vegard's law in all the ranges of substitution. Another way to

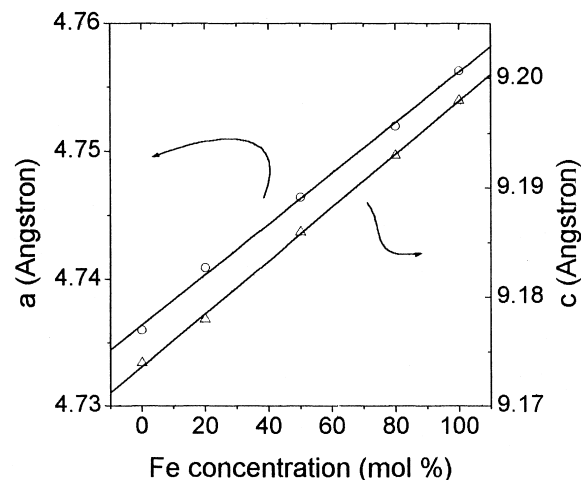


Fig. 2. Variations in unit cell parameters as a function of chemical composition. The solid lines are linear fits of the experimental data.

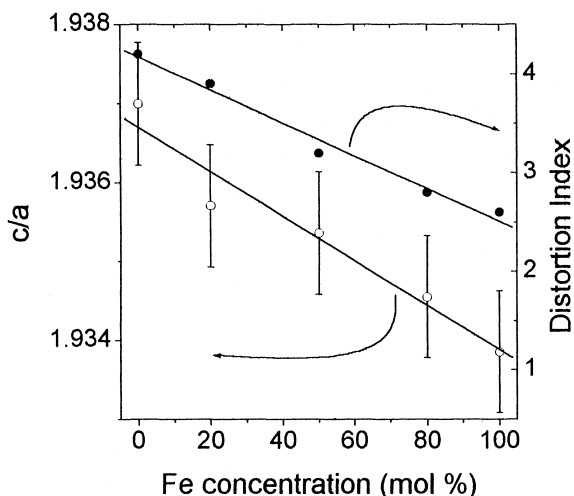


Fig. 3. Variations of the c/a ratio and of the distortion index as a function of chemical composition. The solid lines are linear fits of the experimental data.

appreciate the crystal evolution is by plotting the c/a ratio and the distortion index, DI [17], as a function of Fe concentration. These plots are shown in Fig. 3. The data used to calculate the parameters DI are shown in Table 4. As can be seen, the c/a evolution is quite correlated to that of DI. Although the data follow linear relations within the experimental errors, we can observe small deviations, mostly for c/a , in the region of Fe concentration below 30 mol%, suggesting a different regime for crystal evolution dominated by the Co atoms. It is reasonable to expect that such a behaviour will also be observed on the magnetic properties. In spite of the fact that this discussion is not the aim of the present paper, it is instructive to advance some preliminary magnetic susceptibility measurements performed with a SQUID magnetometer at temperatures ranging from 5 to 300 K, in an applied field of 500 G. There is an outstanding consistence between the X-ray and susceptibility results. As can be seen in Fig. 4, the $T(\chi_{\max})$ dependence on the Fe concentration clearly suggests two different regimes with a boundary at about 30 mol% Fe. Detailed investigation

Table 4

Selected bond distances and distortion indices for $\text{Fe}_x\text{Co}_{1-x}\text{Ta}_2\text{O}_6$

$$\text{DI} = \frac{(\text{O1-O1}) - (\text{O2-O2})}{(\text{O}_i\text{-O}_i)} \times 100$$

x	O1-O1 (Å)	O2-O2 (Å)	DI (%)
0.0	4.0765(80)	4.2451(75)	4.2
0.2	4.0302(84)	4.1890(78)	3.9
0.5	4.1028(77)	4.2367(73)	3.2
0.8	4.1741(93)	4.2935(88)	2.8
1.0	4.2083(138)	4.3201(132)	2.6

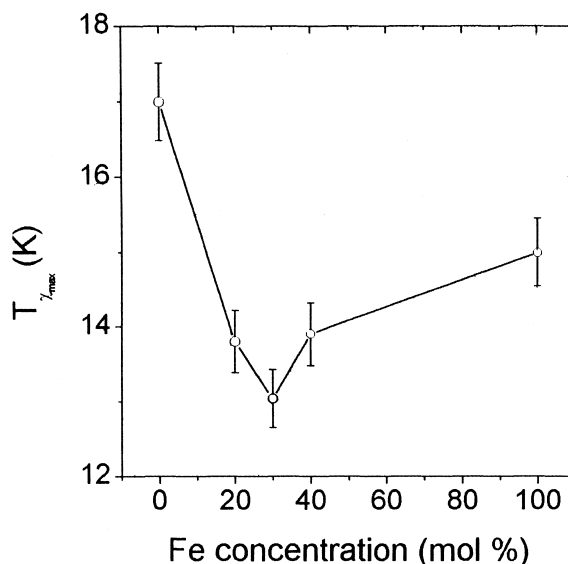


Fig. 4. Temperature at the maximum of the magnetic susceptibility curve as a function of chemical composition. The solid line is a guide to the eyes.

with $0.2 < x < 0.4$ is in progress to analyse this specific question.

In summary, high purity $\text{Fe}_x\text{Co}_{1-x}\text{Ta}_2\text{O}_6$ samples were prepared by a solid-state reaction procedure for $0 \leq x \leq 1$. The cell parameters a and c are linearly related to x , obeying the Vegard's law in all the range of substitution. Although the distortion index and c/a ratio dependence on Fe concentration are linear within the experimental errors, a small deviation is observed for the sample with $x = 0.2$, suggesting the existence of two regimes for the crystal evolution.

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