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THERMAL DECOMPOSITION OF MIXED TITANIUM-CHROMIUM OXYHYDROXIDES.

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ABSTRACT

Crystallographic shear phases of mixed rutile-type oxides $Ti_{n-2}Cr_2O_{2n-1}$ have been prepared for the first time from the thermal decomposition of mixed oxyhydroxides $Ti_{1-x}Cr_xO_{2-x}(OH)_x$ with the InOOH-type structure.

INTRODUCTION

The thermal decomposition of solids is usually an interesting route to prepare mixed oxides. Well known examples are the preparation of mixed Ca-Mn oxides with the mixed carbonates as precursors (1). When the normal oxidation states of both cations are different, it is seldom possible to have a common structure for the precursors. However, in the case of the Ti-Cr system the formation of a mixed oxyhydroxide of titanium (IV) and chromium (III) have allowed us to arrive, at relatively low temperatures, to mixed crystallographic shear phases based on the rutile structure.

EXPERIMENTAL

The starting oxyhydroxides have been prepared by high pressure synthesis from TiO_2 and CrO_2 heated at 1000 °C and 60 kbar in a Belt-type apparatus. Full details of the procedure are given in reference (2). The obtained materials have been characterized by X-ray powder diffraction using a Guinier camera with manganese-filtered FeK_α radiation. Electron diffraction and microscopy were performed on a Siemens Elmiskop 102 microscope operated at 100 kV. T.G.A. experiments were realized in a 951 Dupont Thermogravimetric Analyzer.

RESULTS AND DISCUSSION

All samples can be fitted to the formula $Ti_{1-x}Cr_xO_{2-x}(OH)_x$ with $0 < x < 0.3$. They all show a X-ray pattern characteristic of the InOOH type structure (3). Figure 1 shows the evolution of the unit cell parameters as a function of the composition. It can be observed that while the c parameter, Fig. 1b, remains almost constant, the orthorhombic distortion, as given by $a \neq b$, increases

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in a practically linear way with the value of x. This is a clear reflection of the way in which the hydrogens intervene in the distortion. These hydrogens

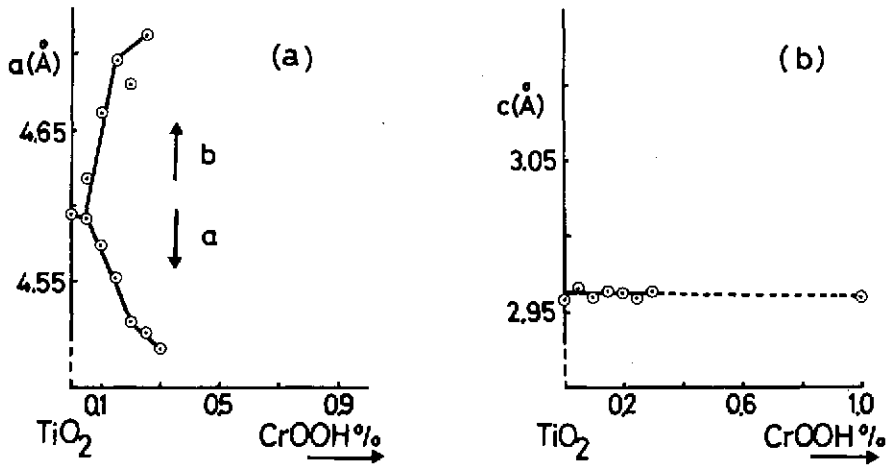

Fig. 1. Evolution of the unit cell parameters as a function of the composition.

are situated within the tunnels that, parallel to the c axis, exist in the rutile type structure (S.G. Pmnm)(4). With the hydrogen in position $(\frac{1}{2},0,\frac{1}{2})$, hydrogens bonds are formed between central octahedra and corner octahedra. Due to this bonding the octahedra tilt around an axis parallel to the c axis of the unit cell.(See Fig. 2).

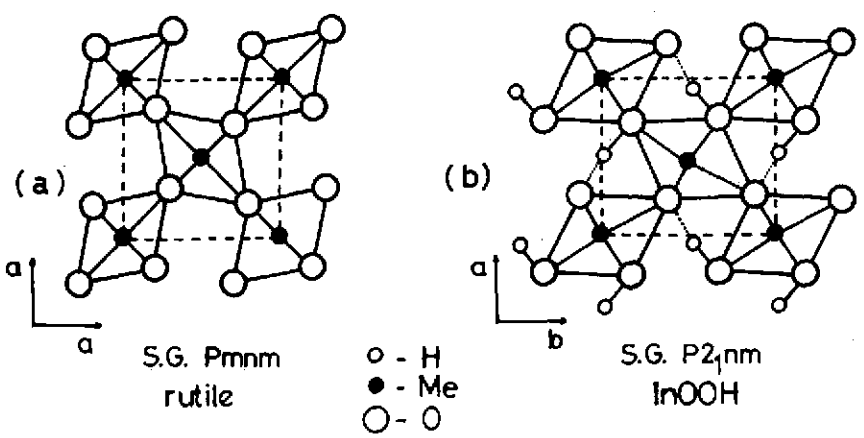

Fig. 2. (a) Projection of the rutile-type structure along the c axis of the tetragonal cell. (b) Projection of the InOOH type structure along the c axis of the orthorhombic cell.

Thermal decomposition of these samples at 1000C in air, using a heating rate of 2°/min, indicates a weight loss around 700C whose values are summarized in Table I. As can be seen they show good agreement with the calculated ones for a water loss according the reaction:

$$Ti^{4+}_{1-x}Cr^{3+}_{x}O_{2-x}(OH)_{x} \longrightarrow Ti^{4+}_{1-x}Cr^{3+}_{x}O_{2-x/2} + x/2\ H_2O \qquad (I)$$

TABLE I

Thermogravimetric analysis of the mixed oxyhydroxides.

x	W(% exp.)	W(% calc.)*	Final composition
0.10	1.09	1.12	$Ti_{0.90}Cr_{0.10}O_{1.95}$
0.15	1.62	1.67	$Ti_{0.85}Cr_{0.15}O_{1.925}$
0.20	2.20	2.22	$Ti_{0.80}Cr_{0.20}O_{1.90}$
0.25	-	-	$Ti_{0.75}Cr_{0.25}O_{1.85}$

* Calculated according to eqn (I).

X-ray powder diffraction of the resulting phases gave very complex patterns characterized by groups of lines located around the normal rutile reflections, indicating that all these solids are superstructures of the rutile structure (5).

To gain a deeper information electron microscopy and electron diffraction were performed on the same samples. Figure 3a shows the pattern corresponding to the $Ti_{0.8}Cr_{0.2}O_{1.90}$ sample. Two 10-fold superstructures along $\bar{g}_{121}$ give unequivocal evidence of the family of cristallographic shear phases (C.S.P.)ba-

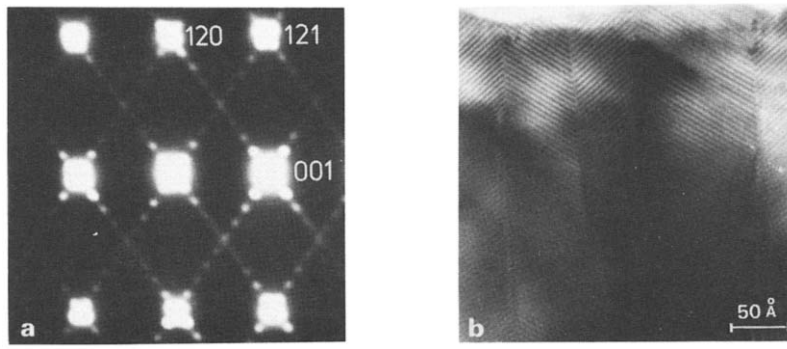

Fig. 3. (a) ED pattern of the x = 0.2 sample showing two 10-fold superstructures along $\bar{g}_{121}$. (b) Corresponding electron micrograph.

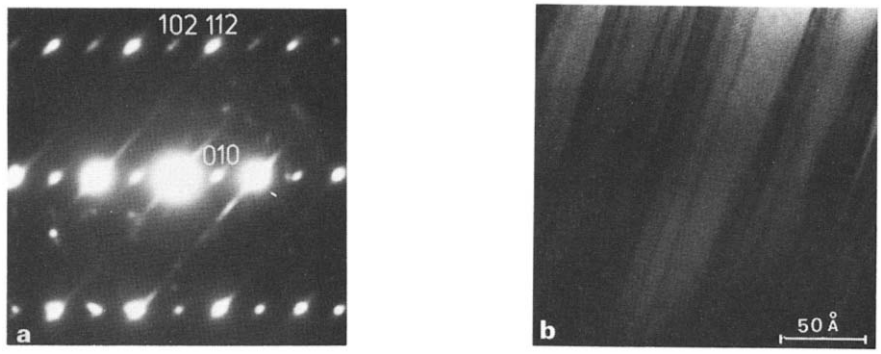

Fig. 4. (a) ED pattern of the x = 0.1 sample along $[20\bar{1}]_r$ zone axis. (b) Corresponding electron micrograph.

sed on the rutile cell and whose composition can be expressed by the general formula $Ti_{n-2}Cr_2O_{2n-1}$ where $n = 2/x$, (x being the value given above for the chromium content). The corresponding electron microscope image, Figure 3b, shows that the two superlattices occur aperiodically in a twinned fashion. When the amount of chromium was of the order of x = 0.1 the corresponding C.S. planes although are all parallel to the (132) planes -in analogy with what happens in reducing TiO_2 (6)- they appear disordered as shown by the streaking observed along the $\bar{g}_{132}$ vector in reciprocal space, Figure 4a, and indeed in the electron microscope image, Figure 4b.

The thermal decomposition of the mixed oxyhydroxides is then an interesting route to prepare C.S. phases of the mixed rutile-type oxides.

REFERENCES

1 K.R. Poeppelmeier, M.E. Leonowicz, J.C. Scanlon, J.M. Longo and W.B. Yelon, J. Solid State Chem., 45 (1982) 71.
2 M.P. Herrero Fernández, J. González Calbet, M.A. Alario-Franco, M. Pernet and J.C. Joubert, Mat. Res. Bull (in press).
3 M.S. Lehmann, F.K. Larsen, F.R. Poulsen, A.N. Christensen and S.E. Rasmussen, Acta Chem. Scand., 24 (1970) 1622.
4 H.D. Megaw, Crystal Structures: a working approach, New York, 1973, 39 pp.
5 O.W. Flörke and C.W. Lee, J. Solid State Chem. 1, (1970) 445.
6 L.A. Bursill and B. Hyde, Progr. Solid State Chem. 7 (1972) 177.