Synthesis of Pure and Mixed Double Oxides with the Ilmenite Structure

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Synthesis, hexafluorotitanates, ilmenites

A new method for synthesizing double oxides of the ilmenite and perovskite type via aquafluoro-complexes $\text{M}^{\text{II}}(\text{H}_2\text{O})_x\text{AIVF}_6$ has now successfully been applied to dilute solid solutions of iron (II) magnesiumtitanates $\text{Fe}_2\text{Mg}_x\text{TiO}_4$. Chemical analysis and X-ray powder diffraction analysis of lattice spacing shifts of different compositions warrant the conclusion that random solid solutions of mixed double oxides can be obtained by the chosen method, with the special advantages of stoichiometry and lower reaction temperatures than in previously described methods.

Thermal decomposition in oxidizing or reducing atmosphere – depending on the kind of cation(s) in the resulting oxide – of some aquafluorotitanates yields ilmenites or perovskites, as illustrated in the following scheme

$$\text{FeCl}_2.4\text{H}_2\text{O} + \text{H}_2\text{TiF}_6.\text{aq} = \text{Fe}(\text{H}_2\text{O})_6\text{TiF}_6$$
$$\text{Fe}(\text{H}_2\text{O})_6\text{TiF}_6 = \text{FeTiO}_3 + 6\text{HF} + 3\text{H}_2\text{O}$$

In this contribution the synthesis and analysis of mixed aquafluoro-complexes and double oxides is described for $\text{Fe}_2\text{Mg}_{1-x}\text{TiO}_4$ with different values of $x$.

Experimental

The synthesis of $\text{Fe}(\text{H}_2\text{O})_6\text{TiF}_6$ from $\text{FeCl}_2.4\text{H}_2\text{O}$ and an aqueous solution of $\text{H}_2\text{TiF}_6$ has been described earlier. The magnesium complex was prepared by adding solid $4\text{MgCO}_3.\text{Mg(OH)}_2.x\text{H}_2\text{O}$ (with known magnesium content) to the warm $\text{H}_2\text{TiF}_6$ solution. Some precipitation already took place before all magnesiumcarbonate had been added. After complete crystallisation in a refrigerator the complex was again filtered and washed with acetone. In preparing mixed complexes of the type $(\text{Fe}_2\text{Mg}_{1-x})(\text{H}_2\text{O})_6\text{TiF}_6$ the solids were first mixed in a mortar in the desired proportions and then precipitation took place before all reactant had been added. After standing in a refrigerator the gel-like precipitate was again filtered and washed with cold acetone. The mixed complexes and the magnesium complex are fine powders, whereas the iron complex consists of pale yellow needles.

Because of the many possibilities of interferences during chemical analysis the main features of the chosen method are given here:

The complexes were freed from fluoride by melting with potassium pyrosulphate (which is also applicable for dissolving the ilmenite oxides) after which the melts were dissolved in dilute sulphuric acid for Ti- and Mg-analysis and in dilute hydrochloric acid for Fe-analysis, respectively. Iron was determined iodometrically, titanium gravimetrically as $\gamma$-hydroxyphenylarsionate. Magnesium was titrated with EDTA after masking of Fe and Ti by adding aqueous solutions of cyanide and triethanolamine.

The results are given in Table I.

Of course these methods of chemical analysis were not accurate enough to establish the correct value of $x$ in the $\text{Fe}_2\text{Mg}_{1-x}$ compounds, which may have a deviation of $5-10\%$, or even higher in the $x=0.015$ compound. However, together with the X-ray powder diffraction data of the oxides, described hereafter, the authors have sufficient reason to conclude that this method of synthesis does yield pure random solid solutions of the oxides.

Decomposition of the complexes to the desired oxides was performed in the usual way: Powdered quantities of 1–2g of the complex in quartz vessels, the bottom of which was covered with platinum foil to prevent silicon contamination, were heated in an atmosphere of 95% $\text{N}_2$ and 5% $\text{H}_2$ saturated with water vapour by bubbling through water, kept at a temperature of 70–80°C.
After some experiments with different decomposition schemes with varying rates of heating and varying temperatures the following decomposition programme of 4-5 hours duration was found satisfactory: The powder was slowly heated from ambient temperature to 250 °C in 2 1/2 hours and then gradually to 850 °C in 2 hours, kept at this temperature 1/2 to 1 hour and kept in the same atmosphere during cooling. For the pure iron complex longer heating periods up to 8 hours were usually applied. The colours of the oxides were black for pure FeTiO₃ and varying from brown-violet to gray for the different mixed oxides, to white for MgTiO₃.

The products were examined by X-ray diffraction of the powders and checked for absence of contaminants such as MgF₂, MgTi₂O₆, TiO₂, etc. The seven strongest lines of the diffraction patterns of two solid solutions (20 and 5% Fe) have been examined by means of a diffraction spectrometer Philips PW 1320-1310. They are given in Table II, together with the corresponding lines of pure FeTiO₃ and MgTiO₃ (ASTM cards no 3-0781, 6-0494, resp.), and mechanical mixtures containing molecular percentages of 20 and 5% FeTiO₃, respectively.

### Table II. Comparison of X-ray diffraction spectrometer data, seven strongest lines of FeₓMg₁₋ₓTiO₃ (x = 0.2 and 0.05) and corresponding mechanical mixtures (20 and 5% FeTiO₃); lattice spacing d in Å.

<table>
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<th>FeTiO₃</th>
<th>MgTiO₃</th>
<th>Mg₁₋₀.₂FeₓTiO₃</th>
<th>Mg₋₀.₀₅FeₓTiO₃</th>
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</table>

### Discussion of Results

The calculated values of d for the solid solutions as given in Table II have been obtained by applying Vegard's additivity rule on the spacings of pure FeTiO₃ and MgTiO₃; This rule states that lattice spacings of solid solutions should vary linearly in proportion to the lattice spacings of the components.

The experimental values appear to be systematically too high, also when compared with the calculated values from the data of the mechanical mixtures. The average deviation is about 5%, but as stated by W. B. Pearson the linearity of Vegard's rule can only be approximate due to non-linear influences on the lattice space fillings of the solid solutions.

The possibility of preferential crystallization of some magnesium aquafluoro complex during the synthesis of the precursors cannot totally be excluded, especially since some crystallization already occurred before all reactant had been
added, as was mentioned in the experimental section. This possible effect, however, did not appear to occur in an appreciable amount. This was checked by powder diffraction on some of the complexes, the diffraction patterns showing only one set of lines. Moreover, in case of a small inhomogeneity of the complex, this will be levelled out during the thermal treatment, giving a homogeneous oxide.

The authors conclude therefore that solid solutions of ilmenites can indeed be synthesized by the aquofluoro-complex method, with the advantage of stoichiometry and lower temperatures during synthesis than in the usual method of heating oxides.

This method also offers the possibility of readily synthesizing very dilute solid solutions of e.g. FeTiO₃ in a MgTiO₃ lattice for spectroscopic (EPR, UV-visible spectroscopy) and magnetic susceptibility investigations. In a preliminary EPR investigation a change in the spectrum was found pointing to a decreased Fe-Fe interaction, thus supporting our conclusion that the dilute oxides are indeed solid solutions.

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7 L. Vegard, Z. Kristallogr. 67, 239 (1928).