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## Preparation of Oxide Solid Solutions by Thermal Decomposition of Tutton's Salts, $(\text{NH}_4)_2\text{M}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (M = Mn, Zn, Fe)

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A recent study of the thermal decomposition of Tutton's salts,  $(\text{NH}_4)_2\text{M}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , in which M represents a mixture of two to six transition elements, showed that when the salts are decomposed in an argon atmosphere the final products of decomposition are solid solutions of metal (2+) oxides but when decomposed in air the resulting solid solutions are metal (2+) and (3+) oxides.<sup>1</sup> Thermal decomposition of Tutton's salts containing a definite ratio of metals in the structure may, therefore, be a route for the synthesis of a homogeneous, uncontaminated reactive powder useful for the preparation of homogeneous magnetic ceramics.

### INTRODUCTION

The crystal structures of Tutton's salts,  $(\text{NH}_4)_2\text{M}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , where M is magnesium or a transition element, were determined in the sixties<sup>2-7</sup> and revealed that the structures are essentially identical. It is obvious, therefore, that the metal ion in a salt can be replaced by another similar metal ion without significant influence on the structure. This was confirmed by our studies of the system  $(\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{O} - \text{MSO}_4$  in which Tutton's salts with two to six different ions in the structure were prepared and investigated<sup>1</sup>. Thermal decomposition of Tutton's salt, where M is a mixture of Mn, Zn, and Fe ions, leads to the formation of MnZn ferrite as the final product, which might be of use in the preparation of high permeability magnetic ceramics.

### RESULTS AND DISCUSSION

For a ferrite powder to exhibit high resistivity together with useful magnetic properties it is necessary to contain a very definite ratio of oxides. An example is a ferrite with 52.5 mol % of  $\text{Fe}_2\text{O}_3$ , 25.5 mol % of MnO, and 22.0 mol % of ZnO in which the composition of ferrite can vary less than 1% with respect to  $\text{Fe}_2\text{O}_3$ . We decided to prepare a Tutton's salt containing these metals in the structure in order to obtain, on thermal decomposition, a ferrite of the above mentioned composition. In the first experiments, an aqueous solution containing  $\text{MnSO}_4$ ,  $\text{ZnSO}_4$  and  $\text{FeSO}_4$  in equi-molar ratio and an excess of  $(\text{NH}_4)_2\text{SO}_4$  were mixed and, after one day, crystals of the formula

$(\text{NH}_4)_2\text{M}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  were produced (sample 1). Its X-ray powder photograph was identical with those of the compounds isolated in previous studies<sup>1</sup>.

The chemical analysis is given in Table I and shows the fraction of the metal ions in the crystallized solids which were separated from the solution.

TABLE I  
Chemical Analysis of  $(\text{NH}_4)_2\text{M}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$

% $\text{NH}_4$	% Fe	% Mn	% Zn	% $\text{SO}_4$	% $\text{H}_2\text{O}^*$
9.1	3.5	1.1	10.7	48.4	27.2

The molar ratio of the components is calculated:

$$\text{NH}_4 : \text{M} : \text{SO}_4 : \text{H}_2\text{O} = 2.05 : 1 : 2.05 : 6.12$$

$$\text{M} = \text{Mn, Fe, Zn}$$

\*  $\text{H}_2\text{O}$  is calculated as the difference to 100.

On thermal decomposition, the final product is a solid solution of oxides ( $\text{Fe}_2\text{O}_3$ ,  $\text{Mn}_3\text{O}_4$  and  $\text{ZnO}$ ) with the composition 15.4% of Fe, 5.5% of Mn and 53.0% of Zn.

On the basis of the chemical analyses of Tutton's salts obtained by mixing the aqueous solutions of metal sulphates in equi-molar ratio, and the solid solution obtained by the thermal decomposition of these Tutton's salts, and the desired composition of the ferrite, we deduced the initial molar ratio of metal sulphates ( $\text{M} = \text{Fe, Mn, Zn}$ ) required for the preparation of sample 2.  $(\text{NH}_4)_2\text{SO}_4$  was used in 50% excess. Green crystals which appeared after eight days were separated from the solution. Several samples were prepared and the chemical analysis of the sample used for the thermal decomposition study is given in Table II.

TABLE II  
Chemical Analysis of  $(\text{NH}_4)_2\text{M}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$

% $\text{NH}_4$	% Fe	% Mn	% Zn	% $\text{SO}_4$	% $\text{H}_2\text{O}^*$
9.2	9.8	2.2	2.5	49.0	27.3

The calculated molar ratio ( $\text{M} = \text{Mn, Fe, Zn}$ ) is:

$$\text{NH}_4 : \text{M} : \text{SO}_4 : \text{H}_2\text{O} = 2.01 : 1 : 2.01 : 5.97$$

\* See footnote of the Table I.

A macrothermogravimetric thermal decomposition on a Mettler thermo-analyzer was carried out to prepare a solid solution of metal oxides. Thermal decomposition in air of sample 1 and sample 2 occurs in the same way which is completely reproducible and characteristic TG and DTG curves are given in Figure 1.

Thermal decomposition of  $(\text{NH}_4)_2\text{M}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  in air begins at 58 °C. Up to 260 °C the sample loses 27.8% of its initial weight and this corresponds to the loss of six moles of water per mole of starting material. The DTG curve exhibits two minima at 122 and 161 °C. In the next step between 260 and

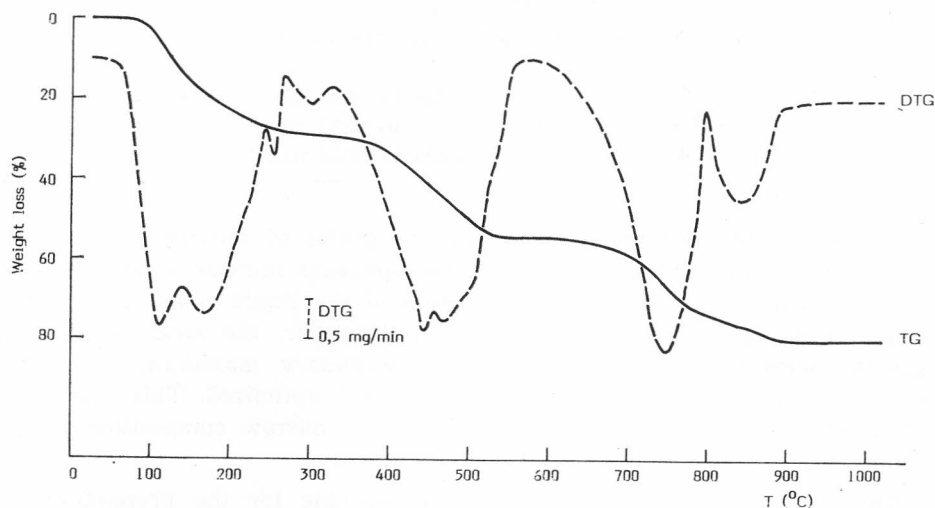
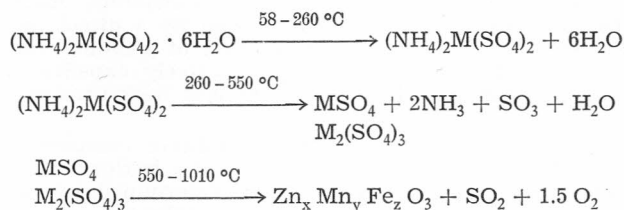


Figure 1. TG and DTG curves of  $(\text{NH}_4)_2\text{M}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  ( $\text{M} = \text{Fe}, \text{Mn}, \text{Zn}$ )

Atmosphere: air  $-5 \text{ l h}^{-1}$   
 Sample weight: 1.13013 g  
 Crucible: Pt  $-3.3 \text{ ml}$   
 Heating rate:  $8^\circ\text{C min}^{-1}$

TG range: 1000 mg  
 DTG range:  $100 \text{ mg min}^{-1}$   
 Ref. substance:  $\alpha\text{-Al}_2\text{O}_3$

$550^\circ\text{C}$  the sample loses a further 26.6% of its weight. At this temperature ammonium sulphate is decomposed<sup>8,9</sup> and metal sulphates remain. This step is accompanied by the DTG minima at 305, 403, 440 and  $467^\circ\text{C}$ . In the last step between 550 and  $1010^\circ\text{C}$  the sample loses 25.4% of its weight and the cumulative weight loss is 79.8%. This corresponds to the formation of a solid solution of metal oxides ( $\text{Fe}_2\text{O}_3$ ,  $\text{Mn}_3\text{O}_4$ ,  $\text{ZnO}$ ). In this temperature interval the DTG curve shows minima at 744 and  $828^\circ\text{C}$ . Thermal decomposition can be described in terms of the following equations:



The composition of the solid solution is given in Table III. After calcination (ferritization) the powders were pressed into toroids and sintered at  $1320^\circ\text{C}$  in oxygen and cooled in a  $\text{N}_2/\text{O}_2$  (1%  $\text{O}_2$ ) atmosphere. In the process of sintering  $\text{Mn}_3\text{O}_4$  is transformed to  $\text{MnO}$ .

The sintered sample exhibited the homogeneous microstructure typical of ferrites without impurities. (In conventionally prepared ferrites appreciable contamination usually occurs during the milling of ferrite powder.) The microstructure of ferrites was inspected by reviewing the polished and etched

TABLE III  
*Chemical Analysis of  $Zn_xMn_yFe_zO_3$*

% Fe = 48.5	corresponds to 51.85 mol % of $Fe_2O_3$
% Mn = 11.8	corresponds to 25.57 mol % of MnO
% Zn = 12.4	corresponds to 22.58 mol % of ZnO

surface of samples. It was observed that the grains of sintered ferrite were uniform in size and shape indicating a homogeneous microstructure. Impurities, if present, would induce the formation of the liquid phase during sintering, triggering anomalous grain growth. However, the measurements of magnetic permeability did not show the secondary maximum, indicating that the composition of the ferrite was not yet optimized. This maximum in magnetic permeability, which is limited to a narrow composition range, is essential for the application of these ferrites.

The method studied was found to be suitable for the preparation of fine grained reactive and homogeneous ceramic powders in which the microstructure was optimal. Furthermore, the ferritization associated with thermal decomposition of Tutton's salts seems to be superior to other methods as far as homogeneity is concerned, since the fluctuation in the chemical composition is limited to the atomic level. However, these advantages are somewhat reduced by the length of the procedure (preparation of crystals and their thermal decomposition).

#### EXPERIMENTAL

*Starting materials.* — 38.85 ml of 1 M solution of  $FeSO_4$ , 1585 ml of 1 M solution of  $MnSO_4$ , 5.30 ml of 1 M solution of  $ZnSO_4$ , and 90 ml of 1 M solution of  $(NH_4)_2SO_4$  were mixed and acidified with sulphuric acid (pH 1.92). The solution was evaporated isothermally at 20 °C and after eighth days the crystals were collected. They were dried in air.

*Characterization.* — Chemical analyses for ammonium, metal and sulphate ions were carried out. Ammonium was determined by a direct method<sup>10</sup> in which a solution of the salt was treated with a solution of sodium hydroxide and then the mixture was distilled. Ammonia was quantitatively expelled and absorbed in an excess of standard acid. The excess of acid was back-titrated in the presence of methyl red.

The sulphate ion was determined by an indirect complexometric titration<sup>11</sup> after addition of concentrated ammonia solution and a buffer solution (pH 10) using Eriochrome Black T as indicator. Metals were determined by atomic absorption spectroscopy<sup>12</sup> in air-acetylene (Zn) and  $N_2O$ -acetylene (Mn, Fe) flames on a Varian AA5 instrument.

X-ray powder photographs of the solids in Pyrex capillaries were taken with Debye-Scherrer and Guinier type cameras and  $CuK_\alpha$  or  $FeK_\alpha$  radiation.

For thermal decomposition in air a Mettler Thermoanalyzer was used. In the macrothermogravimetric experiments approximately 1.2 grammes of Tutton's salt were used.

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## POVZETEK

## Tuttonove soli

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Raziskovali smo Tuttonove soli,  $(\text{NH}_4)_2\text{M}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , v katerih M predstavlja zmes dveh do šestih kovin elementov prehoda<sup>1</sup>. Študij termičnih razkrojev teh soli v atmosferi argona ali zraka je pokazal, da so končni produkti razkroja trdne raztopine kovinskih(2+) oksidov oziroma kovinskih(2+) in (3+) oksidov. Termični razkroj Tuttonovih soli z določenim razmerjem kovin v strukturi je lahko pot za sintezo homogenih, nekontaminiranih reaktivnih prahov, uporabnih za pripravo visoko permeabilnih feritov. Zato smo študirali sintezo  $(\text{NH}_4)_2\text{M}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , kjer M predstavlja zmes Mn, Fe in Zn ionov v določenem razmerju, in termični razkroj te soli v zraku z uporabo rentgenske praškovne analize in termične analize. Ugotovili smo, da zadnja stopnja v tem procesu (feritizacija) vodi do tvorbe homogenega in reaktivnega MnZn feritnega prahu.