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NEW SYNTHESIS ROUTES FOR DIFLUORIDES MF_2 (M = Fe, Mn, Zn AND Ni)

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SUMMARY

Synthesis of pure MF_2 (M = Fe Mn and Zn) by a solid state reaction between the oxides Fe_2O_3 Mn_3O_4 ZnO and ammonium fluoride NH_4F is described Pure NiF_2 is obtained by a liquid phase reaction with aqueous hydrofluoric acid (40%) NiO formed is eliminated with HCl The purities of samples are checked by X ray diffraction magnetic measurements or Mössbauer spectra

INTRODUCTION

Difluoride MF_2 compounds in which M is a transition metal are known since several decades and have been widely studied Generally they are synthesized by reaction of hydrofluoric acid (as gas or in aqueous solution) or F_2 with the metal itself a salt or an oxide[1 4] Chemical processes using other fluorinating agents such as sulfur hexafluoride and tetrafluoride[5 8] ammonium fluoride and molten NH_4HF_2[9 11] have been developed Ammonium double salts were obtained by dissolving MCl_2 chlorides in the latter compound Their decompositions in an inert gas allowed to obtain MF_2 fluorides Recently this method has been extended to zinc and magnesium[10] cobalt and nickel[11] and manganese[12 14] salts The double fluoride salts were prepared from oxides hydroxycarbonates or hydrated double fluorides as starting materials in which the metal was already at the right oxidation state except for zinc[10] To our knowledge synthesis of FeF_2 MnF_2 and CoF_2 fluoride from oxides containing the cation at oxidation states higher than 2 and by using NH_4F as fluorinating agent have never been described Therefore we report on them in this paper Although NiF_2 could be synthesized in this way we prefered a liquid phase reaction with aqueous hydrofluoric acid (HF 40%) allowing us to obtain large amounts of product The reactions are summarized in

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Table I The purities of compounds were checked by X ray diffraction magnetic measurements or Mossbauer spectroscopy

SYNTHESIS OF NiF_2 WITH HYDROFLUORIC ACID AS FLUORINATING AGENT

Nickel(II) hydroxycarbonate powder was dissolved in HF 40% giving a green dark solution which was evaporated The yellow powder obtained as residue was heated at 800 C under vacuum thus giving a mixture of nickel oxide and fluoride The NiO formed was eliminated by a washing with HCl and the resulting powder dried with absolute alcohol After two or three successive heatings at 800 C under vacuum separated by a washing with HCl we obtained pure NiF_2 whose crystallographic parameters are given in Table II Magnetic characteristics of our NiF_2 powder (T_N=73 1K Θ_{WEISS}=151K and C=1 35) were close to those given by Stout and Catalano[15]

TABLE I

Starting materials fluorinating agents and formation temperatures of MF_2 samples

Compound	Starting materials	Fluorinating agent	T(C)
NiF_2	$Ni(OH)_2NiCO_34H_2O$	40% aqueous HF	
FeF_2	Fe_2O_3	NH_4F	750
MnF_2	Mn_3O_4		720
ZnF_2	ZnO		720

SYNTHESES WITH AMMONIUM FLUORIDE AS FLUORINATING AGENT

General procedure

Oxalate or oxides of transition metal M and ammonium fluoride NH_4F (99 9%) taken in a large excess were mixed and ground together The mixture was put in a gold crucible introduced in an inconel tube and kept in a purified argon flow The temperature was first maintained at 150 C for about 15 hours to allow NH_4F and oxides or oxalates to react Then the mixture was heated up at the rate of 3K/mn to the formation temperature T of the fluorides (Table I) The argon rate was slow enough to allow an atmosphere of ammonium fluoride above the crucible during the reaction The samples were then rapidly cooled down to avoid possible oxidations or hydrolysis

Iron fluoride

The intermediate phases encountered were determined for the iron fluoride synthesis using iron oxide as starting compound At 150 C the mixture ammonium fluoride iron oxide reacted and gave a very compact sample The dark claret initial colour changed to pink due to the formation of $(NH_4)_3FeF_6$ When the temperature increased the decomposition of ammonium salt occured and at 250 C we found only NH_4FeF_4 in the sample On further heating the double salt was completely decomposed at about 350 C giving FeF_3 Then the reduction of FeF_3 began with the result that the crucible contained a mixture of FeF_2 and FeF_3 at 400 C Iron trifluoride was then completely reduced at 750 C At temperatures higher than 770 C metallic iron appeared Therefore ammonium fluoride acted first as a fluorinating agent following the reactions

$$Fe_2O_3 + 12\,NH_4F \xrightarrow{\sim 150\ C} 2\,(NH_4)_3FeF_6 + 3\,H_2O + 6\,NH_3$$

$$(NH_4)_3FeF_6 \xrightarrow{\sim 250\ C} NH_4FeF_4 + 2\,NH_4F$$

$$NH_4FeF_4 \xrightarrow{\sim 350\ C} FeF_3 + NH_4F$$

and then reduced FeF_3 Several reactional schemes can be imagined for this reduction for instance these reactions

$$3\,FeF_3 + NH_4F \xrightarrow{\sim 750\ C} 3\,FeF_2 + 1/2\,N_2 + 4\,HF$$

$$3\,FeF_2 + 2\,NH_4F \xrightarrow{>750\ C} 3\,Fe + N_2 + 8\,HF$$

The reducing action of NH_4F was greater at slow flow rates of argon Stopping heating before the last reaction had begun we obtained a white powder whose crystallographic studies showed that it was FeF_2 (Table II) No impurities such as Fe or iron oxide appeared in the Mossbauer spectra at 295K (fig 1) The effective quadrupole splitting 2 79 mm/sec and the isomer shift 1 23mm/sec relative to a Rh source agreed with those given by Wertheim and Buchanan[16] Magnetization measurements definetly proved that our samples were very pure In fact we obtained

$$\sigma(\text{uem}/_{\text{mol}}) = 2\ 55 + 9422\ 10^{6}\ H$$

at room temperature $\sigma_0 = 2\ 55$ uem/$_{\text{mol}}$ showed that less than 0 01% of Fe or Fe_3O_4 was present in our FeF_2 and the susceptibility $\chi = 9422\ 10^{6}$ uem/mol was close to the value given by H Bizette [17] Identical results were obtained even when the starting oxide contained Fe_3O_4

The main problems that we encountered in our method were the formation of Fe_3O_4 when inert gas was not pure enough and the presence of FeF_3 when the quantity of NH_4F was too small In fact a large excess of fluorinating agent was required since the ammonium fluoride was widely hydrated 6 grams of fluorinating agent were necessary to fluorinate and reduce 300mg of iron oxide Fe_2O_3 Note that the water was eliminated when the reaction began and did not interfere in the fluorination

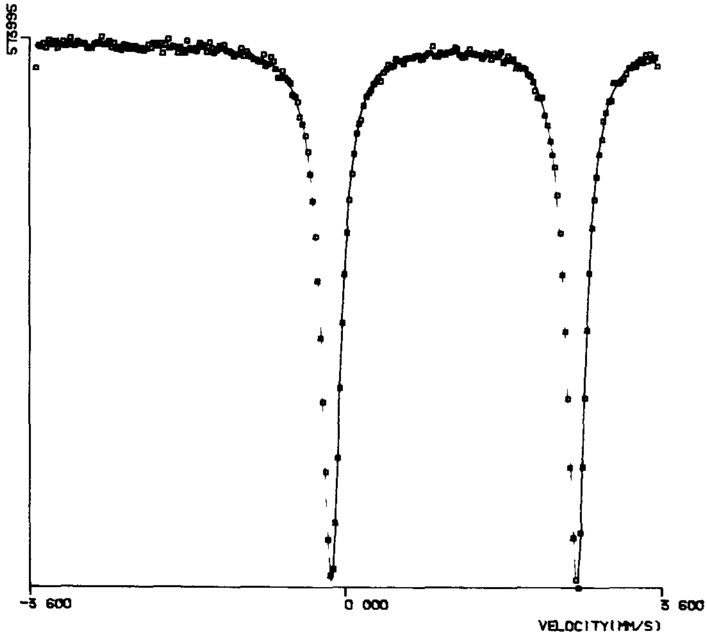

Fig 1 Mossbauer spectra of FeF_2 obtained from Fe_2O_3 and NH_4F

Attempts at synthesizing very pure FeF_2 from iron oxalate failed since the resulting powder contained some carbon (about 1 5 wt %) This carbon arose from the oxalate decomposition the reaction 2CO >C + CO_2 being favoured by the presence of iron

Manganese and zinc fluorides

In the same way white powders of manganese and zinc fluorides MnF_2 and ZnF_2 were obtained using Mn_3O_4 and ZnO as starting materials Similar intermediate phases were encountered But the temperatures at the end of the reactions were different depending on wether the metal could be easily reduced or not (Table I) Metallic manganese and zinc were never found in our samples even at 770 C showing that the stability areas of manganese and zinc fluorides are quite large Crystallographic studies showed that we prepared MnF_2 and ZnF_2 The zinc derivative was pure ZnF_2 as chemical analysis[18] proved calc Zn 63 24% F 36 76% Found Zn 63 60% F 37 53% The purity of MnF_2 was checked by magnetic susceptibility measurements Its magnetic characteristics T_N=71K Θ_{WEISS}=116 8K and C=4 588 close to those obtained by De Haas *et al* [19] and Corliss *et al* [20] showed that it was pure MnF_2 Quite as pure MnF_2 was also synthesized using manganese oxalate as starting material

TABLE II

Comparison between the lattice parameters of our MF_2 samples and those (*) given by W H Baur[21]

Compound	a(±0 005A)	b(±0 005A)	a^*(A)	b^*(A)
NiF_2	4 646	3 085	4 650	3 083
MnF_2	4 867	3 308	4 873	3 309
FeF_2	4 699	3 310	4 696	3 309
ZnF_2	4 700	3 128	4 703	3 133

CONCLUSIONS

Pure fluorides can be obtained either by a liquid phase reaction with a solution of hydrofluoric acid 40% or by a solid state reaction between oxides and ammonium fluoride

The liquid phase reaction is usable when the oxide can be eliminated by an acid or another solvent (case of NiF_2) but unsuitable for fluorides easily hydratable Attempts to obtain zinc fluoride using zinc hydroxycarbonate and a solution of hydrofluoric acid 40% were performed Acetic acid was used successfully in the purification step since ZnF_2 dissolves easily in hydrochloric acid X ray diffraction studies showed that the white powder contained only ZnF_2 but this fluoride hydrates so easily that we cannot state positively that it was pure ZnF_2 This method completely failed for iron manganese copper and cobalt fluorides because of a lack of refining methods

The solid state reaction between ammonium fluoride and metal oxides is more appropriate to obtain pure FeF_2 MnF_2 and ZnF_2 Its main advantages are

practical work is more convenient and less dangerous than experiments with hydrofluoric acid Ammonium fluoride can be recovered in the cold part of the tube

any oxide or mixture of oxides can be used provided that the oxidation states of the metal ion are greater or equal in the oxide than in the fluoride

water does not interfere during the reaction since it is removed before the fluorination begins

However a large excess of fluorinating agent must be used since NH_4F has two functions first it forms with the oxide an ammonium double salt whose decomposition gives a fluoride secondly it reduces the obtained fluoride to give another fluoride as we showed by synthesis of pure FeF_2 The formation temperatures of MF_2 fluorides depend on the ease with which the metal is reduced Probably an accurate control of the reduction process will allow to obtain the wanted fluoride when several fluorides exist for a given metal

Attempts to fluorinate other metal oxides showed that a lot of fluorides can be synthesized by a solid state reaction with NH_4F For instance CuF_2 was obtained by heating a mixture of CuO and NH_4F at 350 C But Cu(II) is so easily reduced and CuF_2 so easily hydratable because of the low reactional temperature that our samples were always blue grey VF_3 was obtained from V_2O_5 at 770 C But the reduction temperature of VF_3 is so high that it was impossible for us to obtain VF_2 In the cobalt case the perovskite type compound NH_4CoF_3 formed with Co_3O_4 always appeared in the X ray diffraction pattern even at 650 C By increasing either the time of reaction or the end temperature cobalt metal was formed even though the perovskite was not completely decomposed This show us that the temperature area for which pure CoF_2 can be obtained is very narrow More accurate studies of temperature areas and technological modifications will have to be done to extend our process to other fluorides

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