

Stabilization of unstable oxides*

C E DESHPANDE and M N SANKARSHANA MURTHY
National Chemical Laboratory, Poona 411 008, India

MS received 3 March 1981

Abstract. Easily oxidizable oxides, FeO, and MnO, are unstable in air but can be easily stabilized by small amounts of other oxides. Further these two unstable oxides stabilize each other very well. Such stabilized FeO and MnO provide easy and reproducible methods of preparing electronic ceramics that need such unstable valency states in them. Ferrous-zinc ferrite has been successfully synthesized employing FeO stabilized with a small amount of Fe_3O_2 .

Keywords. Ferrous zinc ferrites.

1. Introduction

The transition metal oxides, FeO and MnO, are well-known to be highly oxidizable and unstable in air. FeO in fact is so unstable that it usually disproportionates to Fe_3O_4 and Fe. MnO, in a relatively stable form in air, can be obtained if it is sintered and 'dead burnt' at about 1000°C (Hay and White 1934). FeO can also be obtained by decomposition of ferrous oxalate in running vacuum at 850°C and suddenly quenching the material (Lux 1965). These are all elaborate and difficult techniques which are not suitable for the employment of these oxides as 'materials' of any utility in the usual sense of the term. These oxides are certainly needed in the preparation of sophisticated electronic ceramics such as ferrites—for example manganous-zinc ferrites, manganous magnesium ferrites, ferrous-zinc ferrites etc. Because of the difficulty of preparation and handling, these unstable oxides have not been sufficiently explored as catalyst materials; but it is reasonable to expect these transition metal oxides or materials containing them to be valuable as contact catalysts. They would similarly be useful for the removal of oxygen from other gases such as nitrogen. The present investigation describes easy and feasible methods of preparing systems containing these unstable oxides. These oxides can be easily stabilized at relatively low temperatures by solid solutions with very small amounts of other oxides; and furthermore FeO and MnO can be very easily made to stabilize each other in binary systems of FeO-MnO. A binary system FeO- Fe_2O_3 with Fe_2O_3 in small quantities, can also be prepared easily in a stable form.

*NCL Communication No. 2751

2. Experimental

2.1 MnO-ZnO

We have previously reported (Deshpande *et al* 1978) the preparation of this system by heating to 750° C the mixed oxalates in a nominal running current of pure nitrogen and subsequently degassing the material at the same temperature (figure 1). X-ray studies (Deshpande *et al* 1978) showed that zinc oxide dissolves in MnO to the tune of 10 mol %. We have now studied the thermograms of these systems (figure 2) including pure 'dead burnt' MnO and systems rich in ZnO not reported in the earlier paper. The latter systems were also studied by x-ray methods similar to those reported earlier; figure 3 gives the change in ZnO lattice parameters with increasing dissolution of MnO in it. X-ray lines of MnO start appearing only when the molar percentage of MnO in ZnO exceeds 15. We have also previously reported the use of the stabilized MnO in the preparation of manganous-zinc ferrites (Murthy *et al* 1979).

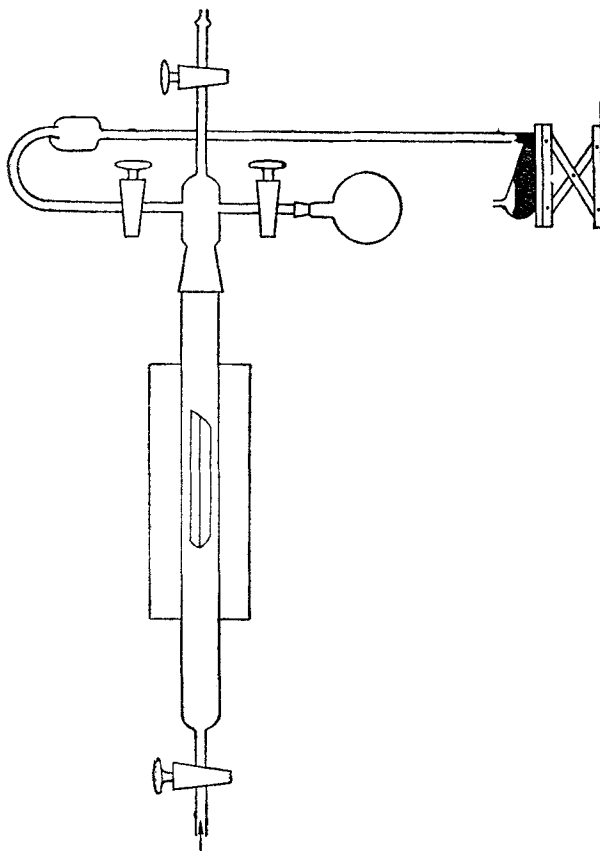


Figure 1. Preparation unit for systems in which FeO and MnO get stabilized.

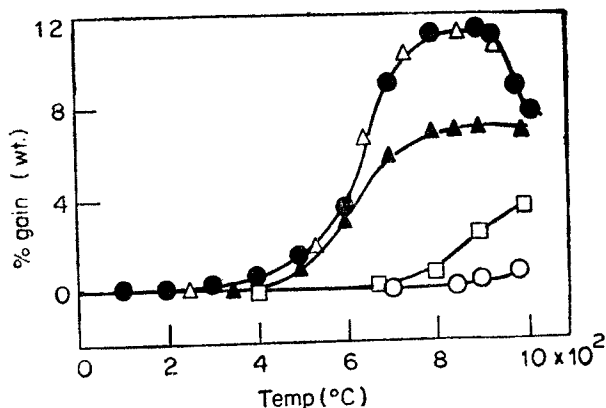


Figure 2. Thermograms of pure MnO●, and binary systems of MnO and ZnO in proportions (a) 99.995; 0.005△, (b) 95:5▲, (c) 50:50□, (d) 20:80○,

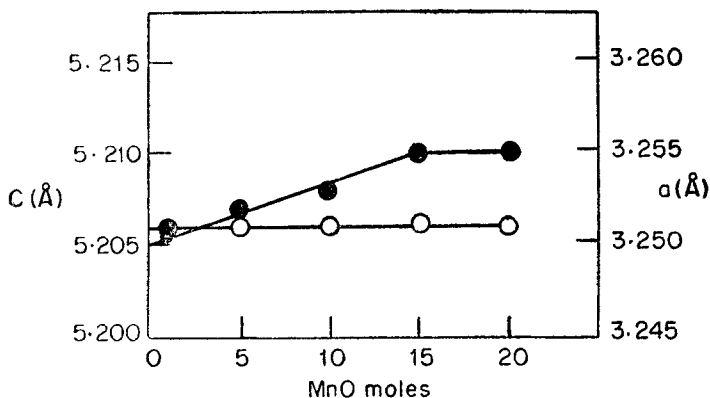


Figure 3. Change in lattice parameter 'C' of ZnO with increasing concentrations of MnO. 'a' does not change. ●—C; ○—a.

2.2 FeO-Fe₂O₃

Active precipitated ferric oxide prepared as described in our paper (Murthy *et al* 1979) was heated for about 8 hr at 950°C in an inert static atmosphere of oxygen-free nitrogen and in the presence of one third its weight of reduced iron. The iron, however, was kept out of contact with Fe₂O₃ to avoid physical contamination. The arrangement was as shown in figure 1 but without the running current of pure nitrogen. On cooling, the material analysed to 62.17 weight percent Fe²⁺ in the material containing 76.88 weight percent of total iron. The material was totally free from iron metal as shown by chemical and x-ray methods. The x-ray powder patterns showed intense lines of FeO (with a slightly shifted cubic lattice parameter) along with only a feeble indication

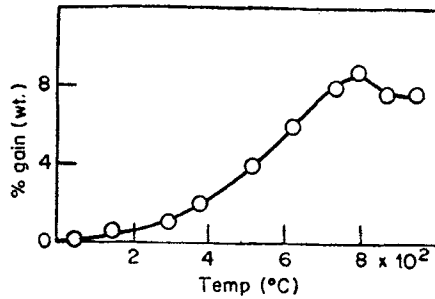


Figure 4. Thermogram of $\text{Fe}_{(1-0.0874)}\text{O}$

of only the most intense line of Fe_3O_4 . The composition works out to $\text{Fe}_{(1-0.0874)}\text{O}$. Its thermogram in air is given in figure 4. After keeping this material for 9 months exposed to air, it analysed to $\text{Fe}_{(1-0.1118)}\text{O}$.

$\text{Fe}_{(1-0.0874)}\text{O}$ (A) as prepared above was mixed thoroughly with ZnO (B) and Fe_2O_3 (C) as shown in table-1 so as to correspond to a series of ferrous-zinc ferrites. The mixtures were pelleted and heated to 1000°C for 12 hrs in a closed system and in pure nitrogen at a low pressure of ~ 18 cm of Hg. The experimental arrangement is given in Murthy *et al* (1979). The starting low pressure of the static nitrogen atmosphere in the unit prevented any bubbling out of gases and consequent loss of oxygen on heating. On cooling, the pellets were ground well and x-ray powder patterns were taken using $\text{FeK}\alpha$, radiation in order to confirm the formation of a single phase spinel as also to study the shift in the cubic lattice parameter with change in zinc concentrations as shown in figure 5. The powder was granulated with 2% of camphor dissolved in alcohol and pressed at about 1.25 tons/cm² so as to yield toroids with about 2 cm O. D., 1 cm I. D. and 0.5 cm thickness. The camphor was carefully

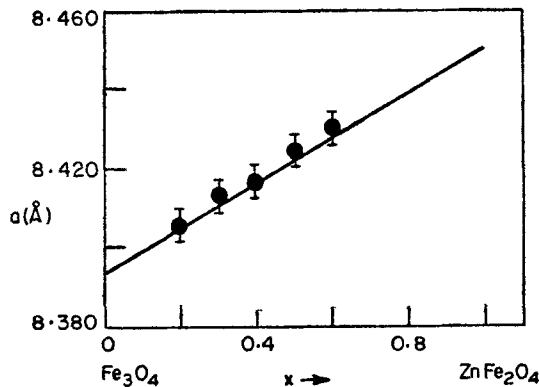


Figure 5. Variation of cubic lattice parameter of $\text{Zn}_x\text{Fe}_{3-x}\text{O}$ with zinc concentration.

Table 1. Details of ferrous-zinc ferrites prepared out of stabilized FeO.

S. No.	Composition	Proportions by wt. of different ingredients taken in gms.			Cubic lattice parameter ^a	μ_i	Q at 800 kHz	μQ
		A	B	C				
1.	Zn _{0.2} Fe _{2.3} O ₄	3.5933	0.8138	7.2656	8.405	75.96	30.5	2316.78
2.	Zn _{0.3} Fe _{2.7} O ₄	3.1442	1.2207	7.3555	8.413	91.33	25.0	2283.25
3.	Zn _{0.4} Fe _{3.6} O ₄	2.6950	1.6276	7.4455	8.416	165.00	17.5	2887.50
4.	Zn _{0.6} Fe _{3.3} O ₄	2.2458	2.0345	7.5354	8.425	229.50	11.4	2616.30
5.	Zn _{0.6} Fe _{2.4} O ₄	1.7966	2.4414	7.6254	8.430	298.00	5.75	1713.50

distilled off below 200°C in a flowing current of oxygen-free nitrogen. The toroids were then sintered in N_2 under a low pressure of ~ 18 cm of Hg at 1270°C for 8 hr in the unit mentioned above (Murthy *et al* 1979). The heating and cooling were done at about 40°/hr. The toroids were wound and initial permeabilities at 800 kHz were computed from the inductance measured on Hewlett Packard Q meter (4342 A) which also measured the Q.

2.3 FeO·MnO

It was of obvious interest to study the system FeO-MnO and find out whether these two oxides, unstable by themselves, could be easily made to stabilize each other by solid solution. So Fe_2O_3 and Mn_2O_3 were thoroughly ground together in proportions mentioned in table 2 and heated at 950°C for about 12 hr in an inert atmosphere and in the presence of an excess of reduced iron (kept out of physical contact with the experimental material) as indicated in figure 1 and described in § 2.2. The resulting materials on cooling gave the results indicated in table 2. The x-ray powder patterns of these systems indicated only the lines of FeO in the iron-rich compositions and those of MnO in the manganese-rich compositions. The lattice parameters were however slightly shifted and compositions with the two components in comparable amounts gave single cubic lattice parameters intermediate in magnitude to those of pure MnO and pure FeO as shown in figure 6. Only composition (10) with 99 mol % of FeO faintly indicated only the strongest line of Fe_3O_4 .

2.4 FeO·ZnO

Similar methods of preparation were tried for this system. The x-ray powder patterns indicated mostly Fe_3O_4 , $ZnFe_2O_4$ besides free ZnO in zinc rich

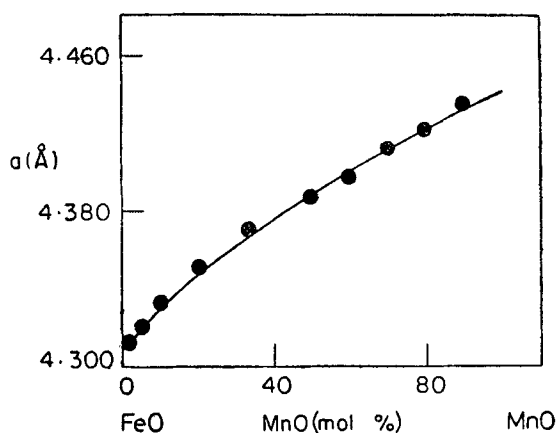


Figure 6. Variation of cubic lattice parameter of FeO·MnO with composition.

Table 2. Details of FeO, MnO systems

S. No.	Starting mixture in moles Fe ₂ O ₃ : Mn ₂ O ₃	% reduction of Mn ₂ O ₃ to MnO	% reduction of Fe ³⁺ to Fe ²⁺
1.	10:90	100	100
2.	20:80	100	100
3.	30:70	100	100
4.	40:60	100	99.55
5.	50:50	100	98.00
6.	66.66:33.33	100	97.56
7.	80:20	100	94.22
8.	90:10	100	90.35
9.	95:5	100	89.77
10.	99:1	100	88.81
11.	100:0	-	80.86

compositions. Even the strong lines of FeO were barely noticeable in iron-rich compositions. An alternative method of preparation, wherein mixed ferrous and zinc oxalates were heated to 950°C under running vacuum and then cooled gradually to room temperature, gave considerable amounts of free iron and Fe₃O₄.

3. Discussion

3.1 MnO-ZnO

The thermograms (figure 2) show that even traces of ZnO stabilize MnO up to 250°C while pure MnO starts absorbing oxygen right from room temperature

Table 3. Uptake of oxygen by the system MnO, ZnO on heating in air. This decreases with increasing ZnO content.

S. No.	Composition MnO:ZnO mole %	% increase in the wt. of solid solution from T. G.	expected % increase in wt. of the sample assuming oxidation of MnO to	
			Mn ₂ O ₃	Mn ₃ O ₄
1	100-0	11.375 at 850°C 7.625 at 1000°C	11.277	
2	99.975-0.025	10.166 at 850°C 7.000 at 970°C	11.274	7.158
3	95-5	7.000 at 855°C	10.635	7.516
4	50-50	3.6 at 1000°C	5.252	7.09
5	30-30	0.833 at 1000°C	2.018	3.501
				1.345

onwards. The minimum temperature of oxidation of MnO increases considerably with the concentration of ZnO even up to 750°C. Table 3 gives the percent increases in weight of the systems MnO:ZnO on heating in air computed from the thermograms as against the expected increases. These calculations show that pure MnO gets oxidized to Mn_2O_3 which subsequently decomposes to Mn_3O_4 at a higher temperature. The uptake of oxygen by the MnO decreases with increasing content of ZnO in it. The composition (3) with 5 mol % of ZnO seems to oxidize directly only to Mn_3O_4 while composition (5) with 80 mol % of ZnO does not seem to give Mn_3O_4 even up to 1000°C.

It is well-known that MnO chemisorbs oxygen with a large heat of chemisorption (Hayward and Trapnell 1964) and the local heat initiates further oxidation of MnO. Probably the active sites responsible for this initial chemisorption of oxygen on MnO are blocked by zinc substitution so that spontaneous chemisorption of oxygen and subsequent oxidation of the MnO are hindered. Figure 3 shows that MnO dissolves in ZnO to the extent of 15 mol %.

3.2 $FeO \cdot Fe_2O_3$

The simple preparative technique described in § 2.2 can yield a compound $Fe_{(1-0.0874)}O$ which is almost pure FeO and can be easily handled at room temperature. The formula of this compound is not to be taken literally since the extent of reduction of Fe^{3+} to Fe^{2+} depends by and large on the activity of the iron powder used as the oxygen-getter. However, the thermogram (figure 4) of this material shows that it starts absorbing oxygen slowly on keeping and this was confirmed. The material is quite stable for at least a week at room temperature and can be used in the mean time for preparing stabler compounds needing even large quantities of Fe^{2+} .

This material was successfully used for preparation of ferrous-zinc ferrites for which very elaborate methods have been described in the literature (Stuijts *et al* 1971). The method is simple and the difference between the attempted and actually prepared compositions was within experimental errors of routine chemical analysis of total iron, Fe^{2+} iron and zinc. The quantities of Fe^{2+} and Fe^{3+} were taken correctly at the start since it was possible to stabilize the former. The binder used was a volatilizable one which could be distilled off below 200°C without having to burn it. Also the calcination and the sintering were done under conditions in which no gases could bubble out of the system even at the higher temperatures of these operations. All these features of the present technique have obviously ensured that the valencies of iron taken at the start remained in tact and as such right up to the end of the final sintering process. This is an advantage over the earlier methods (Stuijts *et al* 1971; Srivastava *et al* 1976) wherein all the iron was inevitably taken as Fe^{3+} and then thermally reduced to the required extent in a flowing current of pure nitrogen at the higher temperatures until the correct amount of oxygen was flushed off as estimated in the outgoing gases. The change

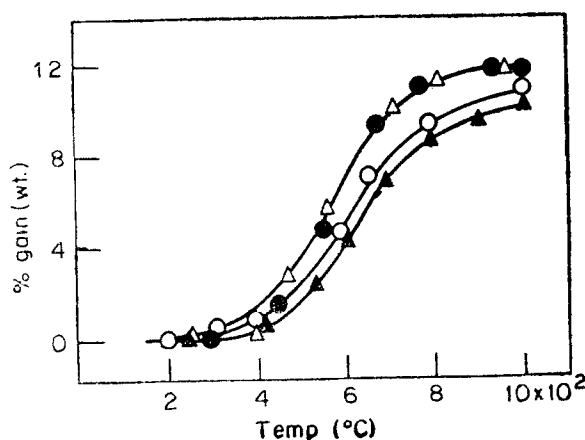


Figure 7. Thermograms of binary systems FeO-MnO in proportions (a) 99:1 O; (b) 95:5 ▲; (c) 50:50 △; (d) 20:80 ●.

in the cubic lattice parameter of the spinel agrees with that reported carrile (Miyata 1961). Further work on this material is in progress.

3.3 FeO-MnO

Section 2.3 above gives a very simple method of preparing these binary systems for which very difficult preparative methods have been employed earlier (Foster and Welch 1956). Systems rich in MnO are totally free from Fe^{3+} whose concentration gradually increases as the FeO content in the system increases. Even the system with 99 mol % of FeO shows faintly even the strongest line of Fe_3O_4 . The thermograms (figure 7) show that the stabilization of FeO with MnO is very good. Even the system mentioned above with the highest FeO content is stable up to 200°C. This seems to be by far the best way of stabilizing FeO. It is remarkable that while both FeO and MnO are so unstable in air, they stabilize each other so well. Another interesting point that can be seen from the above preparations is that Fe_2O_3 gets reduced to a larger extent in the presence of Mn_2O_3 than when alone (table 2). Apparently Mn_2O_3 acts as a catalyst in the reduction of Fe_2O_3 .

3.4 FeO-ZnO

The simple method used for the above systems does not seem to succeed for this system for which probably more elaborate methods are required. Also ZnO seems to hinder considerably the reduction of Fe_2O_3 to FeO (in the presence of reduced iron as oxygen getter) probably due to the formation of ZnFe_2O_4 which is more difficult to reduce. In fact, ZnFe_2O_4 x-ray lines were seen in the reduced material.

4. Conclusions

We have worked out simple methods of stabilizing the highly unstable oxides FeO and MnO. These stabilized oxides, FeO and MnO, render the preparation of electro-ceramics such as manganous-zinc ferrites and ferrous-zinc ferrites easy, free from uncertainty and highly reproducible. The required amount of Fe or Mn can be taken in the bivalent state itself right from the start instead of having to reduce thermally the stabler Fe^{3+} or Mn^{3+} , at the temperature of calcination or sintering, with a flowing current of inert gas. Because of the difficulty of stabilizing these oxides their catalytic properties have not been studied much and the present technique of easy stabilization of these oxides at relatively low temperatures may be of interest in contact catalysis.

Acknowledgement

The authors are grateful to Dr L M Pant for helpful discussions in the x-ray part of the work. Many thanks are due to Dr V G Gunjkar for taking the thermograms and Mr J S Gujral for the x-ray diffractograms. Grateful thanks are also due to Mr P P Bakare and Mrs J J Shrotri for general help in the work.

References

- Deshpande C E, Pant L M and Murthy M N S 1978 *Indian J. Chem.* **A16** 251
Foster P K and Welch A J E 1956 *Trans. Faraday Soc.* **52** 1626
Hay Howat and White 1934 *J. West of Scotland, Iron Steel Inst.* **41** 97
Hayward D O and Trapnell B M W 1964 *Chemisorption* 2nd ed.
(London: Butterworths) Po. 85 table 8,
Lux H 1965 *Handbook of preparative inorganic chemistry* 2nd ed.
(ed) G Brauer (New York: Academic Press) Vol. 2, p. 1497
Miyata N 1961 *J. Phys. Soc. Jpn.* **16** 1291
Murthy M N S, Deshpande C E, Bakare P P, Shrotri (Mrs) J J
1979 *Bull. Chem. Soc. Jpn.* **52** 571
Srivastava C M, Shringi S N, Srivastava R G and Nanadikar N G 1976
Phys. Rev. **B14** 2032
Stuijts A L, Veeneman D and Broese Van Groenou A 1971 *Ferrites*,
Proc. Int. Conf. Japan, 1970 (eds.) Y Hoshino, S Iida and M Sugimoto
(Tokyo: University of Tokyo Press) p. 236