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Reactive sintering of zinc ferrite

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The reactive sintering of zinc ferrite, i.e. firing without previously calcining, has been studied using three types of iron oxide. The conversion into ferrite as well as the simultaneous densification were investigated upon variations in morphology and impurity content. The formation reaction is shown to be accompanied by a strong increase of the median pore size. This phenomenon appears responsible for the generally smaller density of the final material as compared with single-phase sintering. It is shown that reactive sintering is inevitably accompanied by expansion, irrespective of molecular volume variations. A calcining step appears indispensable for the preparation of the highest quality of ferrites.

1. Introduction

The most vital step in the processing of a ceramic is the sintering of the powder compact into the final product. During this process the microstructure of the material is developed which determines to a great extent its performance. Reactive (or: reaction) sintering stands for the concurrent processes of reaction(s) and densification during firing [1, 2]. A reaction in this sense may be the formation of the intended product [3–5], but the term is also used when oxidation–reduction reactions [5], phase transitions [6], or the formation of a solid solution [7] or a liquid phase [8, 9] are involved. In this way reactions caused by impurities or additives, which are often included in the "normal" sinter process, in fact imply some sort of reactive sintering.

Densification during sintering is usually brought about by the lowering of the surface free energy through elimination of solid–vapour interfaces by material transport. The decrease in free energy in a chemical reaction, however, is much larger [1, 10] – and may also be accompanied by a diffusion flow [11]. The occurrence of such a reaction could be expected to affect the densification behaviour and microstructure development.

Ferrites are a good example of compounds which undergo chemical reactions during sintering. For instance after calcining, the reactants are usually only partly converted into ferrite and full formation has to take place during the subsequent sinter process. As a rule, the aim is to achieve the highest possible conversion after calcining [12]. However, the chemical composition *during* sintering is only rarely considered. Chemical reactions that have taken place [5] may thus remain unnoticed. To investigate the pure effect of the conversion, zinc ferrite is a suitable model system, which has already been investigated thoroughly [13–26]: the conversion takes place at a relatively low temperature without the risk of a subsequent decomposition. The objective of this paper is limited to evaluating the effects of the formation reaction on the development of the microstructure during sintering.

The problem in analysing such a process is the separation of effects due to a particular reaction from those originating from (e.g.) impurities or inhomogeneities. For example, a local excess of iron oxide induces extra cation vacancies [27], which strongly affect the densification behaviour. In order to identify such complications three types of iron oxide and three ferrite compositions were examined.

2. Experimental procedure

Two commercial iron oxides were used: one from BASF and a Ruthner type iron oxide from Hoogovens (Ijmuiden, The Netherlands). As they differed both in particle size and impurity content, BASF iron oxide was calcined in air at 700° C to a material with a specific surface area comparable with that of the Ruthner Hoogovens iron oxide. This calcining procedure did not increase the impurity content of the BASF iron oxide, except for a slightly higher silicon level. The zinc oxide used was a very pure material from UCB (Union Chimique Belgique, Drogenbos, Belgium). Table I presents the relevant data of all reactants. In Fig. 1 SEM photographs give an impression of the morphology of the reactant materials. Three ferrite compositions, $Zn_{1-x}Fe_{2+x}O_4$ with $x = 0$, 0.03 and 0.10, were compared to detect effects of the amount of excess iron oxide.

Mixing was performed by ball-milling in an isopropanol slurry which did not induce any detectable conversion into spinel or change of the specific surface area. In the following the mixtures of the different iron oxides with the zinc oxide will be designated by the code letters (A), (B) and (C) as in Table I. Isostatically pressed (100 MPa) tablets were fired (heating rate: $120° C h^{-1}$, 4 h at top temperature) in a double-pipe furnace in which nitrogen could be flushed between inner and outer tubes to prevent air from leaking in. The sinter atmosphere was flushed at $2 l min^{-1}$ and consisted usually of air. Occasionally a temperature-dependent amount of oxygen was applied according to [28]: $\log p_{O_2} = -12\,140/T + 8.70$ with p_{O_2} in % of atmosphere and T in K.

TABLE I Raw materials

Property	ZnO	Fe_2O_3*		
		(A)	(B)	(C)
A(m^2 g^{-1})†	3	20	2.5	3
D_N (μm)‡	0.4	0.06	0.5	0.4
Purity§	99.99	99.96	99.96	99.5
Na	< 0.01	< 0.01	< 0.01	0.02
Si	< 0.001	0.002	0.003	0.009¶
Ca	< 0.001	< 0.001	< 0.001	0.009
Mn	0.0001	0.01	0.01	0.2
Ni	< 0.001	0.002	0.002	0.03
Cl	< 0.001	< 0.001	< 0.001	0.085

*(A) BASF iron oxide; (B) BASF iron oxide calcined at 700° C in air; (C) Ruthner iron oxide.
† Specific surface area from BET.
‡ Particle size from A.
§ By spectrochemical analysis in wt % (unless otherwise indicated).
¶ By chemical analysis in wt %.

The (reaction) sintered samples were characterized by:

(i) density: if over 90% theoretical density by water displacement, otherwise from the dimensions or from mercury porosimetry (Carlo Erba 2000, Milan, Italy) experiments;

(ii) conversion into spinel: by measuring (calibrated) peak heights from X-ray diffraction;

(iii) microstructure: if less than 85% dense, by mercury porosimetry or by scanning electron microscopy (SEM) of a fracture surface; otherwise by observing the polished etched surface.

In separate experiments the densification in air was monitored by dilatometry (Netzsch 402 ES single push-rod dilatometer).

3. Results

The size of the particles as observed from SEM photographs of the raw materials (see Fig. 1) agreed with the data obtained from specific surface area measurements (see Table I). Neither the oxygen content of the sinter atmosphere nor the excess amount of iron oxide were found to have any effect on density, microstructure, or conversion after reaction sintering at temperatures below 1100° C, i.e. before the final density was reached. Consequently, no further specifications in this respect are given.

The conversion into spinel in sintered samples as a function of the sinter temperature (i.e. the top temperature) is shown in Fig. 2, while the corresponding densities are plotted in Fig. 3. A comparable but more distinct picture of the densification behaviour was obtained by means of dilatometry, the results of which are given in Fig. 4. In Fig. 4a the direct densification curves reproduce the expansion of the (C) mixture, observed already in Fig. 3 for samples after sintering. The (B) mixture too showed a clear expansion now, which appears smoothed in Fig. 3. An even more distinct picture was obtained by plotting the derivative of the densification curves (Fig. 4b): now all three mixtures display a comparable maximum around the temperature at which the conversion took place. The obvious conclusion is that the formation reaction is in all cases accompanied by expansion.

To obtain more insight into the development of the microstructure during the first stages of densification, the samples were analysed by mercury porosimetry. In Fig. 5 the median pore size obtained from these experiments is plotted against the sinter temperature. Especially in the case of the (B) and (C) mixtures it can be seen that an increasing conversion (cf. Fig. 2 and Table II) is accompanied by an (extra) increase of this pore size. Concurrently, the specific surface area is decreasing, which implies an increase of the average particle size, D_N, (see Table II). SEM pictures of fracture surfaces confirmed the still distinct particle morphology (without appreciable neck growth) after sintering below 1000° C (Fig. 6).

The essential point, however, is the implication of these parameters with respect to the final density and microstructure. To this end we calcined (4 h at 800° C in air) part of the mixtures and sintered pressed pellets of both calcined and non-calcined powders. Fig. 7 shows typical results of the microstructures thus obtained. The final pore size is strongly reduced by the calcining procedure. No significant variations of this trend were observed between the results of the (A), (B) and (C) mixtures.

4. Discussion

It is well known that the powder characteristics of the raw materials influence both the conversion and the sintering of ferrites [21–25]. The (B) mixture with the coarser iron oxide, however, showed the same temperature dependence for the conversion as the (A) mixture (see Fig. 2). At first sight this is in contrast with an earlier report [23], but in that case the particle size variations were not only larger but should probably be ascribed indeed rather to differences in vacancy concentration of the reactant materials than to a particle size effect. Furthermore, it should not be precluded that the absence of a difference between the (A)

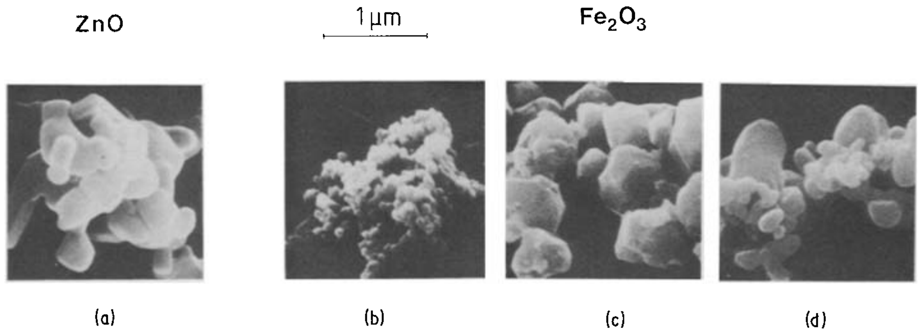

Figure 1 SEM pictures of the UCB zinc oxide and the iron oxides: (a) BASF iron oxide; (b) as (a) but calcined at 700° C in air; (c) Ruthner iron oxide.

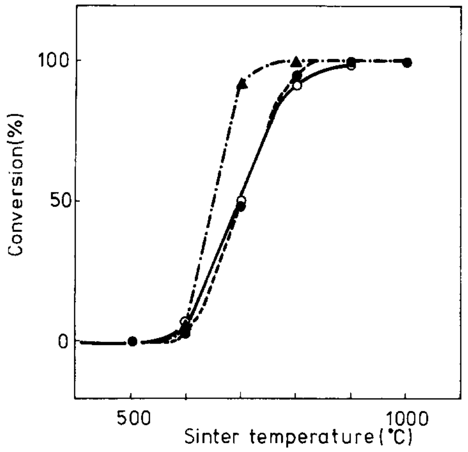

Figure 2 Conversion into spinel of sintered pellets as a function of sinter temperature: (○) (A) mixture, (●) (B) mixture, (▲) (C) mixture.

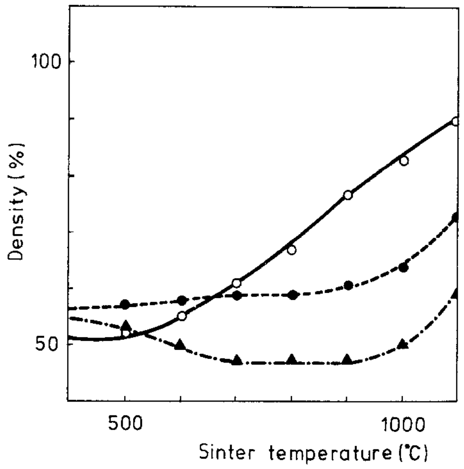

Figure 3 Density of sintered pellets as a function of sinter temperature: (○) (A) mixture, (●) (B) mixture, (▲) (C) mixture.

and (B) mixtures is caused by the strong degree of agglomeration of the fine particles in the (A) mixture (cf. Fig. 1). The (C) mixture with the both coarser and less pure iron oxide, on the other hand, showed conversion into spinel at a lower temperature. Either a better mixing [25] is obtained with this iron oxide (e.g. because of the apparently more rounded particles as shown in Fig. 1), or the increased conversion is caused by the presence of (some of the) impurities. Indeed, it has been shown before [29] that (e.g.) chloride impurities may enhance the conversion into spinel. A volatilization of iron in the form of ferric chloride might be involved here [30].

The densification is much more strongly influenced by the morphology: the temperature at which the densification starts increases with the particle size. With the (C) mixture, however, an additional increase of this temperature (Figs 3 and 4) was found. Better mixing and thus stacking of the particles would have been expected just to improve the densification characteristics, so in this case only the presence of (some of the) impurities appears a likely cause of the observed differences. At the moment, we do not know what impurities are effective, nor the mechanism(s) by which they operate. From the results presented in Figs 3 and 4 it is clear that the formation reaction is always accompanied by macroscopic expansion. Even when an expansion *seems* absent, as in the case of the (A) mixture, this is only because of interference between densification (starting already at a lower temperature) and expansion (during reaction).

The concurrence of a large initial expansion with a chemical reaction – or, more generally, with interdiffusion – is not uncommon [4, 31–35]. Sometimes an expansion can simply be explained by an increase of the average molar volume [32, 34], but with the formation of zinc ferrite from the oxides this is not the case: the average density of a mixture of zinc oxide and iron oxide, $5.35\,\mathrm{g\,cm^{-3}}$, is almost equal to that of zinc ferrite, $5.34\,\mathrm{g\,cm^{-3}}$ [36]*. In the comparable formation of zinc aluminate, it has been suggested [4, 34] that the product phase would separate the original reactant grains before they had disappeared. However, it is not necessary to assume such a mechanism to explain the expansion. A Kirkendall effect of unequal diffusion flows would cause an increase of the porosity (and hence of the volume) in the faster diffusing species [31, 33, 37]. In the extreme case of diffusion of only one component an expansion should also be expected. Consider a system of spheroid equimolar particles of iron oxide and zinc oxide. A bcc-like stacking of these with Fe_2O_3 at the vertices and ZnO in the centre, would result in an expansion of already more than 10%. The reason obviously is a less

TABLE II Characteristics of sintered (C) mixture pellets

T (°C)*	ϱ ($\mathrm{g\,cm^{-3}}$)†	α (%)‡	$r_{p,50}$ (μm)§	A ($\mathrm{m^2\,g^{-1}}$)¶	D_N (μm)ᵃ	$D_N/r_{p,50}$
–	2.82	0	0.100	3.40	0.33	3.3
600	2.70	5	0.135	2.91	0.38	2.8
650	2.59	48	0.184	2.40	0.46	2.5
700	2.55	92	0.246	2.11	0.53	2.1
800	2.55	100	0.291	1.57	0.71	2.4
900	2.50	100	0.317	1.43	0.78	2.5
1000	2.66	100	0.341	1.22	0.92	2.7

*The sample was heated 4 h in air at this temperature.
†Density of the sample determined from its weight/volume ratio.
‡Conversion from calibrated X-ray diffraction peak heights.
§Median pore radius from mercury porosimetry.
¶Specific surface area from BET.
ᵃThe particle diameter from A according to $D_N = 6/(\varrho_x A)$, where ϱ_x is the theoretical density.

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*This is contrary to the (unreferenced) values suggested by Lesniewski *et al.* [35].

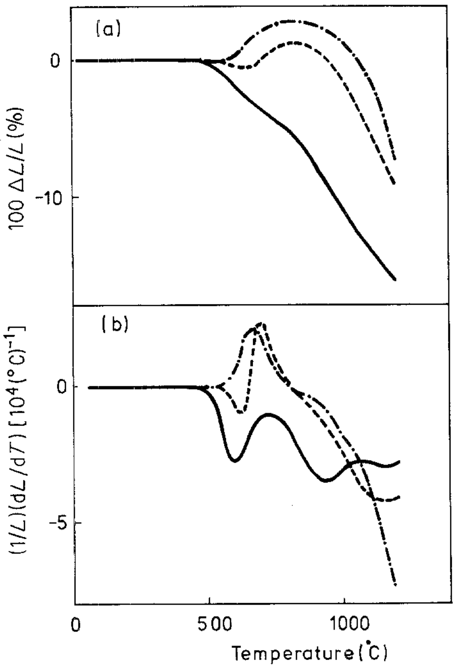

Figure 4 In situ densification as measured with dilatometry: (a) densification curves, (b) derivatives of the densification curves. (——) (A) mixture, (– – –) (B) mixture, (–·–·–·–) (C) mixture.

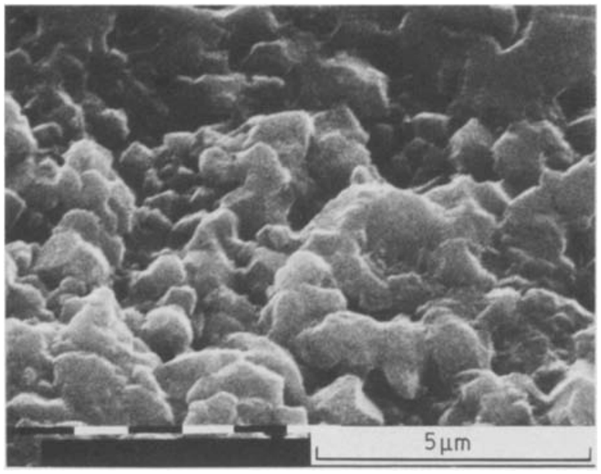

Figure 6 Microstructure after sintering at 1000° C in air of an (A) mixture, showing still a clear particle morphology.

ideal filling-up of the space. Anyhow, in practice a macroscopic expansion appears to be almost inevitably linked with reactive sintering in the sense of concurrent formation reaction and densification.

Pore growth is also a well-known phenomenon during the sintering of single-phase ceramics. Whittemore and Sipe [38] showed that neck growth during the first stage of sintering would account already for an increase of 45% of the original value of the pore diameter after compaction. Even an increase by a factor of two or three, as in our results, is not uncommon [39–40]. Several effects may be involved here. The microstructure after reactive sintering (as shown in Fig. 7) is not unlike that after sintering a material with a large excess of iron oxide [39]. A local excess could be conceived from the *a priori* inhomogeneity of reactive sintering, although one would have expected then an influence of the amount of overall excess – which was not the case, as stated above. Other effects that may be held responsible are (e.g.) the inhomogeneous densification caused by a broad particle size distribution [41, 42], or the occurrence of the already mentioned Kirkendall porosity by unequal mutual diffusion of the reactants [10, 33, 37].

This (extra) increase of the pore size could have severe consequences with respect to the microstructure after sintering. It has been shown that the ability for a pore to be removed during sintering is determined by its size [43], or, more accurately, by its pore coordination number, i.e. the number of particles surrounding the pore [44]. Above a certain critical value of this number the pore cannot be removed, which sets a limit to the attainable density. An impression of this pore coordination number can be obtained by considering the ratio of particle size and pore size, $D_N/r_{p,50}$ in Table II – provided that the compacts compared do not differ in extent of neck growth. The higher this ratio, the smaller the (average) number of particles surrounding the pores. In experiments with a single-phase material this number gradually increases with proceeding densification. However, with the (C) mixture it clearly *decreased* concurrent with the formation reaction (see Table II). As a result, the average pore coordination number is increased, and hence the number of pores which cannot be removed during sintering. This could lead to the very large pores in Fig. 7. Anyhow, an increase of the porosity appears to be an inherent phenomenon of reactive sintering. An improvement of this process might be expected from a more gradual densification (in time) by "rate-controlled sintering", but this would not principally counteract any of the effects described above.

When the formation reaction precedes densification, reactive sintering will therefore always result in a lower density. On the other hand, if the densification precedes the reaction this will probably happen inhomogeneously and induce stresses and pore growth [2, 37, 42, 45] owing to differences in morphology and inherent properties of the reactants. It is not surprising then that the microstructure after "green sintering" is

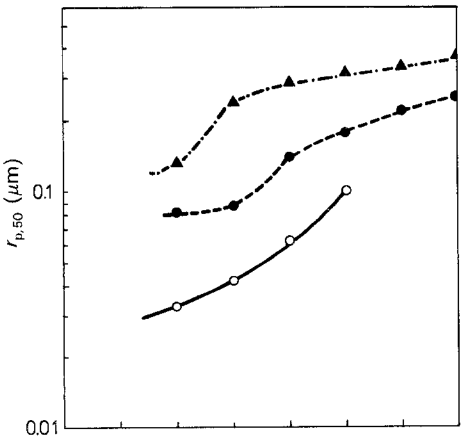

Figure 5 Median pore size from mercury porosimetry as a function of sinter temperature: (○) (A) mixture, (●) (B) mixture, (▲) (C) mixture.

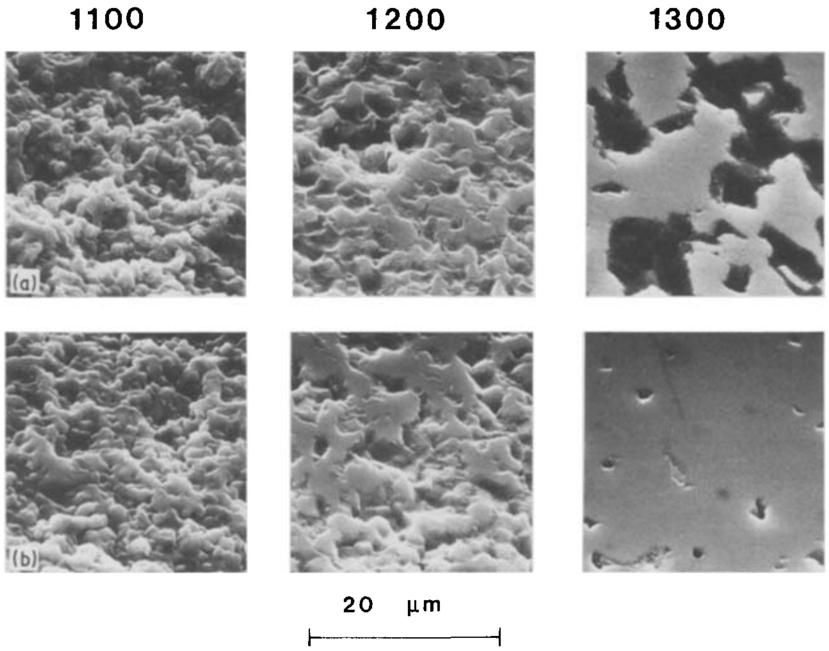

Figure 7 Microstructure after sintering in air at the temperatures indicated above (°C): (a) non-calcined (C) mixture (= reactive sintering). (b) calcined (C) mixture.

generally characterized by a lower density and larger pores, as seen in Fig. 7. Comparable results upon variation of sinter and calcining temperature have been shown before for manganese–zinc ferrites [5]. An improvement of the microstructure can only be expected in the suppression of discontinuous grain growth, caused (and hence inevitably accompanied!) by the larger pores which stick more strongly to the grain boundaries. To minimize the increase in pore size during the reaction, the best results would seem achievable with homogeneously mixed particles smaller than those applied in this report.

5. Conclusions

Reactive sintering of zinc ferrite is always accompanied by a macroscopic expansion and an increase of the average pore size. The reason is that the simultaneous process of formation reaction and densification will decrease the homogeneity of the compact. With the materials investigated in this report a calcining step appears essential to obtain the homogeneity required for preparing high-quality ferrites.

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References

1. D. KOLAR, *Sci. Ceram.* **11** (1981) 199.
2. SHEN YANGYUN and R. J. BROOK, *Sci. Sintering* **17** (1985) 35.
3. M. TRONTELJ and D. KOLAR, *Special Ceram.* **6** (1975) 39.
4. C. LEBLUD, M. R. ANSEAU, E. di RUPO, F. CAMBIER and P. FIERENS, *J. Mater. Sci* **16** (1981) 539.
5. F. J. C. M. TOOLENAAR, *Solid State Ionics* **16** (1985) 267.
6. L. J. BOWEN, R. J. WESTON, T. G. CARRUTHERS and R. J. BROOK, *J. Mater. Sci.* **13** (1978) 341.
7. F. KOOLS, *Solid State Ionics* **16** (1985) 251.
8. G. ROSSI and J. E. BURKE, *J. Amer. Ceram. Soc.* **56** (1973) 654.
9. F. M. A. CARPAY and A. L. STUIJTS, *Sci. Ceram.* **8** (1976) 23.
10. R. L. COBLE, *Mater. Sci. Monogr.* **14** (1982) 145.
11. D. W. READEY, in "Microstructure and Properties of Ceramic Materials", edited by T. S. Yan and J. A. Pask (North-Holland, Amsterdam, 1984) p. 134.
12. M. A. STRIVENS and G. CHOL, in Proceedings of the 2nd International Conference on Ferrites, Kyoto, 1970, edited by Y. Hoshino, S. Iida and M. Sugimoto (University of Tokyo Press, 1971) p. 239.
13. D. W. HOPKINS, *J. Electrochem. Soc.* **96** (1949) 195.
14. R. LINDNER, *J. Chem. Phys.* **23** (1953) 410.
15. J. F. DUNCAN and D. J. STEWART, *Trans. Faraday Soc.* **63** (1967) 1031.
16. J. BERETKA and M. J. RIDGE, *Nature* **216** (1967) 473.
17. D. ELWELL, R. PARKER and C. J. TINSLEY, *Czech. J. Phys. B* **17** (1967) 382.
18. K. KRISHNAMURTHY, J. GOPALAKRISHNAN, G. ARAVAMUDAN and M. SASTRI, *J. Inorg. Nucl. Chem.* **36** (1974) 569.
19. E. K. BELYAEV, *Izv. Akad. Nauk. SSSR, Neorg. Mat. (En)* **13** (1977) 2031.
20. G. A. KOLTA, S. Z. EL-TAWIL, A. A. IBRAHIM and N. S. FELIX, *Thermochim. Acta* **36** (1980) 359.
21. T. YAMAGUCHI and T. NOMURA, in Proceedings of the 3rd International Conference on Ferrites, Kyoto, 1980, edited by H. Watanabe, S. Iida and M. Sugimoto (Centre for Academic Publication, Japan, 1981) p. 46.
22. M. ITO, M. SENNA and H. KUNO, *ibid.* p. 50.
23. V. BALEK, *Sprechsaal* **117** (1984) 1112.
24. A. FELTZ and A. MARTIN, *Mater. Sci. Monogr.* **28A** (1985) 137.
25. R. FURUICHI, K. TANI, K. KAMEDA and T. ISHII, *Reactivity of Solids* **1** (1986) 309.
26. Y. HAYASHI, T. KIMURA and T. YAMAGUCHI, *J. Amer. Ceram. Soc.* **69** (1986) 322.
27. P. J. L. REIJNEN, *Sci. Ceram.* **4** (1968) 169.
28. V. F. KOMAROV and Yu. D. TRET'YAKOV, *Izv. Akad. Nauk. SSR Neorg. Mater.* **8** (1972) 120 (En.).
29. U. WAGNER, *J. Magn. Magn. Mater.* **23** (1981) 73.
30. F. X. N. M. KOOLS, private communications (1987).
31. G. C. KUCZYNSKI, in "Sintering and Related Phenomena", edited by G. C. Kuczynski, N. A. Hooton and C. F. Gibbon (Gordon and Breach, New York, 1967) p. 685.
32. E. di RUPO, M. R. ANSEAU and R. J. BROOK, *J. Mater. Sci.* **14** (1979) 2924.
33. Y. NAKAMURA, S. CHANDRATREYA and R. FULRATH, *Ceramurgia Int.* **6** (1980) 57.
34. M. R. ANSEAU, E. di RUPO and F. CAMBIER, *ibid.* **16** (1981) 825.

35. A. LESNIEWSKI, S. GASIOREK and R. MOSKALEWICZ, *Sci. Sintering* **11** (1981) 99.
36. Handbook of Chemistry and Physics, 64th Edn, (1983) pp. B101, B156.
37. M. PAULUS, in "Preparative Methods in Solids State Chemistry", edited by P. Hagenmuller (Academic, New York, 1972) p. 487.
38. O. J. WHITTEMORE Jr and J. J. SIPE, *Powder Technol.* **9** (1974) 159.
39. A. L. STUIJTS, *Solid State Ionics* **16** (1985) 108.
40. T. K. GUPTA and R. L. COBLE, *J. Amer. Ceram. Soc.* **51** (1968) 521.
41. M. PAULUS, *Mater. Sci. Res.* **6** (1973) 225.
42. A. L. STUIJTS, in "Ceramic Microstructures '76", edited by R. M. Fulrath and J. A. Pask (Westview, Boulder, Colorado, USA, 1977) p. 1.
43. W. D. KINGERY and B. FRANCOIS, in "Sintering and Related Phenomena", edited by G. C. Kuczynski, N. A. Hooton and C. F. Gibbon (Gordon and Breach, New York, 1967) p. 471.
44. F. F. LANGE, *J. Amer. Ceram. Soc.* **67** (1984) 83.
45. A. G. EVANS, *ibid.* **65** (1982) 497.

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