Letters

Effect of non-stoichiometry on sintering of magnetite

A number of oxides exhibit a wide range of non-stoichiometry. This fact is usually taken into account during sintering studies [1-4] by conducting the experiment in the controlled environment of oxygen. However, little attempt has been made so far to relate the sintering kinetics to the actual deviation from stoichiometry since to do so requires precise knowledge of the phase equilibria between the oxide and the oxygen in the ambient atmosphere [4, 5].

In what follows we investigate the effect of non-stoichiometry on the sintering behaviour of magnetite since its oxygen content is known to be sensitive to the oxygen partial pressure [6-8]. The homogeneity range of the oxide between 1000 and 1500°C is shown in Fig. 1 where the oxygen partial pressure isobars are also superimposed. It is seen that with the selection of appropriate oxygen pressure and temperature, a sample of predetermined stoichiometric variation can be obtained. However, it is not possible to vary the stoichiometry widely below about 1100°C which is almost three-fourths of the melting temperature. Hence, at and above 1100°C, the grain growth is likely to be predominant from the earliest stages of sintering as was subsequently confirmed by the metallographic examination of the sintered samples. It is thus to be expected that in this investigation the grain growth would constrain the sintering rates [9].

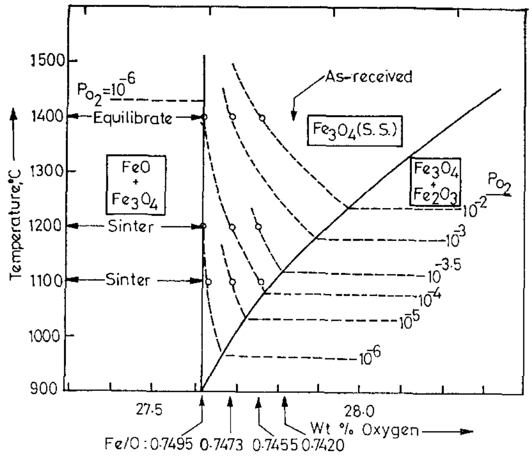

Figure 1 Fe-O phase equilibria near spinel region [8-10]. Dotted lines represent oxygen partial pressure isobars, pressure in atm.

The expediency compelled the use of "purified" grade magnetite with 1 to 2 μm particle size. However, we note that magnetite is impurity tolerant, i.e. the impurities have much less effect on the iron ion diffusivity than do the deviations from stoichiometry [10], permitting the use of impure sample without confusing the kinetic results.

The Fe/O ratio in magnetite was controlled in accordance with the phase diagram by equilibration at 1400°C. Fig. 1 shows the gas mixtures (high purity argon with variable oxygen content) used for equilibration in order to obtain Fe/O ratios of 0.7455, 0.7473 and 0.7495. The minimum equilibration time was determined by holding the powder at 1400°C for increasing times followed by sintering as described below. When constant shrinkage owing to sintering was obtained beyond a certain equilibration time limit, that time was regarded as minimum necessary. For all samples, the equilibration for 2 h at 1400°C was found to be adequate.

The equilibrated material appeared to have sintered to some extent and was ground in an electric ball grinder to yield 2 to 4 μm particle size range. The powder was hydrostatically pressed into 1 in. diameter and ¼ in. thick discs and sintered. The basic equipment used for equilibration and sintering was similar: a platinum wound furnace with an evacuated mullite tube through which the predetermined gas mixture flowed. The thermal equilibrium, as checked by measurements taken on a thermocouple embedded in the centre of the sample, was attained in about 1½ min. The temperature was controlled to within ± 2°C.

For equilibration, the furnace was mounted horizontally, the sample kept in an alumina boat in appropriate atmosphere and after 2 h rapidly quenched by suddenly releasing the boat into liquid nitrogen. The precautions taken to maintain the required atmosphere have been described elsewhere [11]. For sintering, the furnace was mounted vertically and the pressed disc introduced into the heat zone on a platinum hook by means of a winch mechanism. The sintering temperatures of 1100, 1150 and 1200°C for times up to 200 min were used, along with

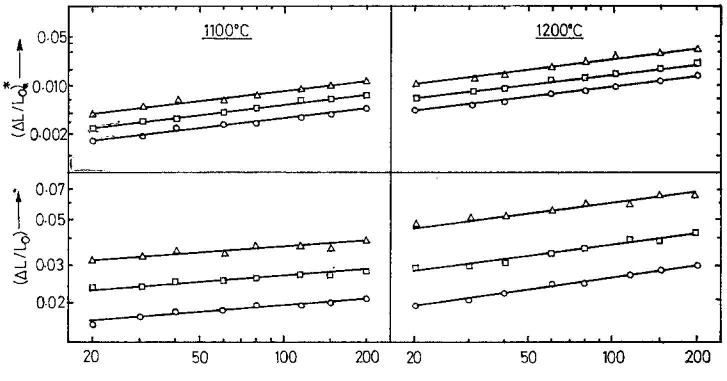

Figure 2 Effect of non-stoichiometry on sintering at 1100 and 1200°C. Note: $(\Delta L/L_0)^* = (\Delta L/L_0) - (L/L_0)_{5\ \text{min}}$, (Fe/O: 0.7490–○–, 0.7473 –□–, 0.7455 –△–).

atmospheres shown in Fig. 1, so as to retain Fe/O ratios obtained during equilibration. Linear shrinkage was measured by interruption of the experiment by quenching in air and by using a micrometer calibrated in ten thousands of an inch.

The results of sintering at 1100 and 1200°C are shown by the two lower set of graphs in Fig. 2. The decrease in the Fe/O ratio, i.e., increase in the deviation from stoichiometry, significantly increases shrinkage. Each sintering curve follows the relation $(\Delta L/L_0) = K\,t^n$ where L_0 is original diameter, ΔL change in diameter and K, n constants. The sintering rate, $(\mathrm{d}/\mathrm{d}t)\,(\Delta L/L_0) = (n/t)\,(\Delta L/L_0)$ changes with time and increases with the stoichiometric deficiency. It is clear that lower sintering temperatures may be employed if sufficient stoichiometric deficiency can be maintained.

The sintering rates are low and the value of n is about 0.10 at 1100°C and 0.15 at 1200°C, attributable to the high temperatures employed. Much of the shrinkage appears to have occurred during the first 5 to 10 min. Although the exact amount of shrinkage during this initial process must remain arbitrary, subtracing the initial shrinkage at 5 min and replotting the remaining shrinkage gives n value of 0.49 at 1100°C and 0.52 at 1200°C as shown by the $(\Delta L/L_0)^* = (\Delta L/L_0) - (\Delta L/L_0)_{5\ \text{min}}$ versus time plots in Fig. 2. The proximity to $n = 0.5$ would immediately suggest diffusion along long paths in the coarse grained structure [12, 13]. The activation energies are readily calculated by plotting ln (n/t) against reciprocal temperature and they are 83, 81 and 79 kcal g.mol^{-1} for Fe/O ratios of 0.7495, 0.7473 and 0.7455 in accordance with the activation energy for self diffusion of iron ion in magnetitite [14].

We assume that two Fe^{3+} ions replace three Fe^{2+} ions causing one cation vacancy and consequently accounting for the decrease in Fe/O ratio. It is now straightforward to calculate the vacancy concentration for each Fe/O ratio. The calculated values, without adding the thermal vacancy concentration of the order of about 10^{-3}%, are 0.01, 0.03 and 0.1% corresponding to the Fe/O ratios of about 0.7495, 0.7473 and 0.7455, respectively. Thus the indications are that the increase in the controlled vacancy concentration increases the sintering rate as well as the total shrinkage [15].

It is instructive to compare these results with the sintering behaviour of the as-received sample. Table I shows the shrinkage of equilibrated and as-received samples at 1100°C for 500 min in $p_{O_2} = 10^{-4}$ atm. The former had been equilibrated so as to yield Fe/O ratio of 0.7455, whereas the latter was in the oxidized state with Fe/O = 0.7420. It is clear that the as-received sample would decrease its oxygen content and approach the equilibrium value of Fe/O = 0.7455, however much slower than at 1400°C. Furthermore, Fe_2O_3 would eventually precipitate, and part or all of sintering would proceed in the presence of the second phase precipitates. The results indicate higher shrinkage for the as-received sample, mostly owing to its finer particle size and higher oxidation state.

Thus equilibration prior to sintering is a critical factor that should be taken into account. An *ad hoc* use of oxygen partial pressure is likely to land the sample in the two phase field and its oxygen content, and hence the defect

TABLE I Shrinkage in equilibrated and as-received samples

Time (min)	1100°C, $p_{O_2} \approx 10^{-4}$ atm.			
	Equilibrated		As received	
	$(\Delta L/L_0)$	$(\Delta L/L_0)^*$	$(\Delta L/L_0)$	$(\Delta L/L_0)^*$
5	0.0239	—	0.1560	—
10	0.0305	0.0066	0.1780	0.0220
50	0.0351	0.0112	0.1842	0.0282
100	0.0410	0.0171	0.1883	0.0323
200	0.0418	0.0179	0.1961	0.0401
500	0.0430	0.0191	0.1992	0.0432

Note: the incremental shrinkage $(\Delta L/L_0)^*$ is given as

$$\left(\frac{\Delta L}{L_0}\right)^* = \left(\frac{\Delta L}{L_0}\right) - \left(\frac{\Delta L}{L_0}\right)_{5\text{ min.}}$$

concentration, would change with time. At low sintering temperatures, the equilibration would be imperceptibly slow and the change in defect concentration would occur only in the surface layer [16]. It is thus imperative that in the non-stoichiometric compounds, the equilibration and the sintering should be separately carried out in the correct atmosphere.

References

1. L. F. NORRIS and G. PARRAVANO, *J. Amer. Ceram. Soc.* **46** (1963) 449.
2. D. H. WHITMORE and T. KAWAI, *ibid* **45** (1962) 375.
3. K. W. LAY and R. E. CARTER, *J. Nuclear Mater.* **30** (1969) 74.
4. K. W. LAY, *J. Amer. Ceram. Soc.* **54** (1971) 18.
5. J. P. ROBERTS and J. HUTCHINGS, *Trans. Faraday Soc.* **55** (1959) 1394.
6. M. W. SHAFER, *J. Phys. Chem.* **65** (1961) 2055.
7. L. S. DARKEN and R. W. GURRY, *J. Amer. Chem. Soc.* **68** (1946) 798.
8. B. PHILLIPS and A. MUAN, *J. Phys. Chem.* **64** (1960) 1451.
9. Y. IIDA and S. OZAKI, *J. Amer. Ceram. Soc.* **42** (1959) 219.
10. C. E. BIRCHENALL, in "Mass Transport in Oxides" (NBS Special Publ. 296, Washington D.C., 1968) pp. 119-127.
11. S. J. BHATT and H. D. MERCHANT, *J. Amer. Ceram. Soc.* **52** (1969) 452.
12. R. L. COBLE, *J. Appl. Phys.* **32** (1961) 787.
13. M. J. BANNISTER, in "Sintering and Related Phenomena" (Gordon and Breach, New York, 1967) pp. 581-605.
14. S. M. KLOTSMAN, A. N. TIMOFEYEV and I. SH. TRAKHTENBERG, *Phys. Met. Metall.* **10** (5) (1960) 93.
15. L. C. F. BLACKMAN, *Ind. Chem.* **38** (1962) 620; **39** (1963) 23.
16. G. C. KUCZYNSKI, in "Powder Metallurgy in Nuclear Age" (Metallwerk Plansee, Reutte, Austria, 1962) pp. 166-79.

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Transparent $Pb_{1-x}La_x(Hf_{1-y}Ti_y)O_3$ electro-optic ceramic

A number of compositions in the lead lanthanum zirconate-titanate (PLZT) solid solution series have been prepared as transparent ceramic materials and have been studied extensively in recent years on account of their potentially useful electro-optic properties [1, 2]. However, there have been few reports of the chemically similar lead hafnate-titanate series [3, 4] and none whatsoever on the system lead lanthanum hafnate-titanate (PLHT), the hafnate analogue of PLZT. In the past this neglect has been attributed to a combination of the relative scarcity of hafnium and the assumption that, by virtue of the chemical similarity of hafnium and titanium, $PbHfO_3$-based materials would behave identically to $PbZrO_3$-based materials in all respects. However, since the hafnium atom is 1.95 times heavier than the zirconium atom whilst having virtually the same ionic radius, it seems likely that there may be substantial differences in phonon-dependent behaviour, e.g. optical and acoustic properties. This letter reports the preparation and preliminary evaluation of a transparent ceramic material having the composition $Pb_{0.90}La_{0.10}Hf_{0.65}Ti_{0.35}O_3$ (PLHT 10/65/35), being the hafnate analogue of a well-known electro-optic zirconate-based material (PLZT 10/65/35).

Transparent PLHT material was prepared in