Acknowledgements

The authors are grateful to Professor R. W. K. Honeycombe for the provision of laboratory facilities. Valuable discussions with Dr. B. Ralph are gratefully acknowledged. Financial support for this work was provided by the SRC and the Springfield Laboratories of the United Kingdom Atomic Energy Authority.

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*Received 15 November
and accepted 19 December 1977*

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Sintering and grain growth in doped ZnO

Recent new uses of ZnO-based ceramics in electronics demand close control of grain size. Although several authors reported on sintering and grain growth of ZnO, the influence of various additives is not yet satisfactorily explained.

On heating ZnO becomes oxygen deficient. Material transport during sintering may be controlled either by the diffusion of Zn^{2+} or O^{2-} ions and the published data support both possibilities [1, 2]. This note reports data which show how the onset of sintering and the grain size of sintered specimens can be influenced by adding a small amount of another oxide.

Experiments were carried out with ZnO p.a.* with a grain size below 1 μm (Fig. 2). Up to 0.5 wt% of TiO_2 and Sb_2O_3 were added as powders, and Li_2O and K_2O were added as aqueous solutions of Li_2CO_3 and K_2CO_3 respectively. The shrinkage curves of cylindrical pellets of 57 ± 1% of theoretical density were determined by the Netzch dilatometer with a heating rate of $300^\circ C h^{-1}$. After reaching 1180° C the samples were anealed for 2 h at this temperature and were examined for density and microstructure.

During the sintering of 0.5% doped ZnO the most remarkable effects are the rapid sintering of Li_2O-doped samples and the shift of the onset of sintering of Sb_2O_3-doped ZnO towards higher temperatures (Fig. 1).

The beneficial effect of Li on the sintering of ZnO was observed previously by Marshal *et al.* [1], who concluded that sintering is controlled by the diffusion of oxygen vacancies through the lattice. On the other hand later studies of the sintering of ZnO [2] showed strong indications that the lattice diffusion of zinc is the rate-controlling step.

The concentration of interstitial zinc ions in ordinary zinc oxide is very small [3]. The incorporation of Li into the ZnO lattice produces Zn-

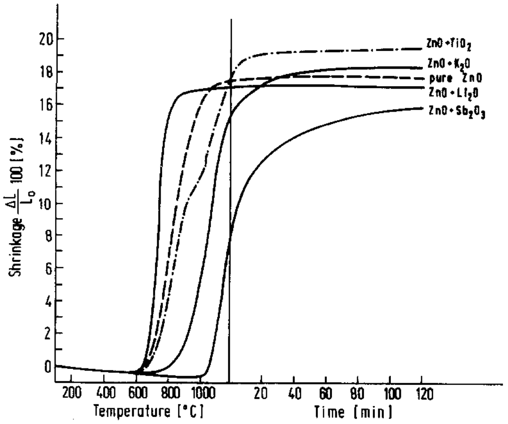

Figure 1 Sintering curves for pure and 0.5% doped ZnO samples.

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*p.a. = pro analysis (equivalent to reagent grade).

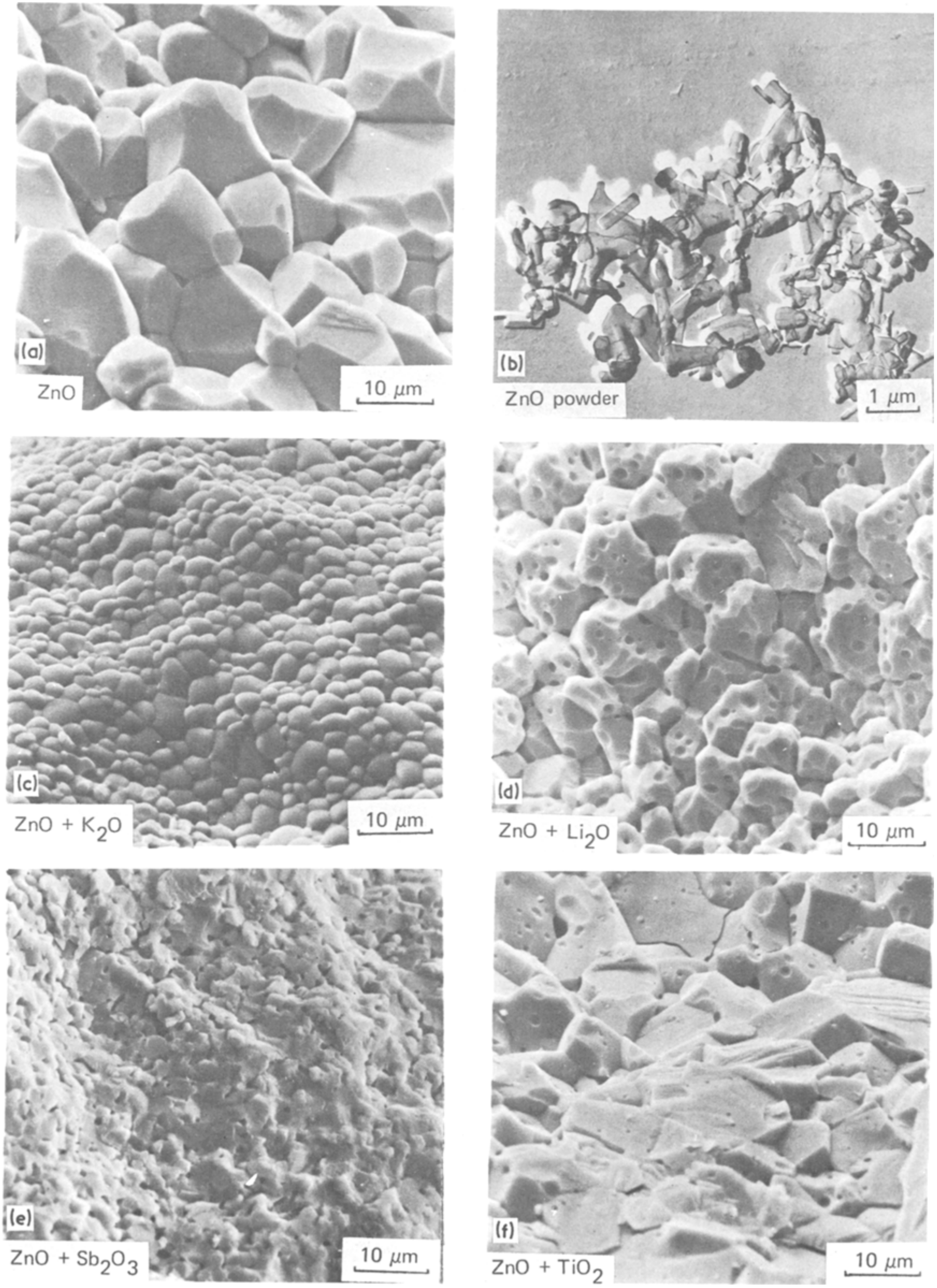

Figure 2 Microstructures of pure and 0.5% doped ZnO samples after firing at 1180° C for 2 h. (a) ZnO; (b) ZnO powder; (c) ZnO + K_2O; (d) ZnO + Li_2O; (e) ZnO + Sb_2O_3; (f) ZnO + TiO_2.

TABLE I Densities and grain size of samples after firing at 1180° C for 2 h

Sample	T_S (° C)*	Density (% of theoretical	Grain size (μm)
ZnO	570	97	16
ZnO + Li_2O	590	97	11
ZnO + K_2O	680	96	4
ZnO + TiO_2	570	98	15
ZnO + Sb_2O_3	790	91	4

*T_S is the temperature at which shrinkage of sample was observed on the sintering curve.

interstitials by displacement of lattice zinc ions by interstitial lithium [4]. A concentration gradient of Zn-interstitials is set up between the surface and the interior of the ZnO particles, which could accelerate sintering.

The K^+ ion is large as compared to Li^+ and it is not likely to be incorporated into the ZnO lattice. The influence of K_2O on the sintering of ZnO is slightly retarding as demonstrated in Fig. 2.

The addition of TiO_2 does not influence sintering significantly at the intermediate stage of sintering, but these samples sintered to higher density than pure ZnO. After twelve hours at 1325° C, a density higher than 99% of theoretical density was achieved. Prolonged heating at this temperature resulted in a decrease in density of all samples. A decrease in density has already been noted in sintering of pure ZnO above 1350° C [5].

The addition of Sb_2O_3 shifts the onset of sintering to 790° C. The density after 2 hours at 1180° C is merely 91% of theoretical density (Table I). Obviously, material transport in Sb_2O_3-doped samples is hindered. It is known that Sb_2O_3 reacts with ZnO to form a $Zn_7Sb_2O_{12}$ spinel phase [6]. This means considerable interdiffusion of Sb_2O_3 and ZnO. Electron probe microanalysis showed Sb-rich reaction zones surrounding ZnO sintered spheres. The new layer of spinel phase can retard the diffusion of zinc through the lattice.

Microstructural comparisons after identical sintering at 1180° C showed that the additives studied always impede grain growth in ZnO as compared with pure samples. Fig. 2 shows the typical microstructure of pure and doped ZnO. Li did not influence the grain size but it strongly influenced pore structure. While in pure ZnO the pores occupy grain corners or lie on grain boundaries, the pores in Li-doped samples are located predominantly within the grains. Such microstructure is typical for fast densification at the intermediate stage of sintering, when pores are trapped in the grains.

The TiO_2-doped sample sintered under identical conditions shows a dense structure. Pores trapped in the grains are small. The solubility of Ti in the ZnO grains could not be detected by electron microprobe analysis. It was observed as a discrete phase along some boundaries of ZnO grains.

Strong inhibition of grain growth was observed in the K- and Sb-doped ZnO. The retarding effect of K_2O on grain growth was observed previously by Gupta [7]. Spectrochemical analysis of the samples after firing showed that Li- and K-doped samples contained only 0.01% of dopants while the loss of Ti and Sb was not observed.

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Received 18 November
and accepted 19 December 1977.

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