

to endorse strongly the type of wide ranging studies that the paper [1] and the other references attempt rather than the narrow studies, often made during ceramics processing (with usually, quite unwarranted generalization of such results).

## References

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P. E. D. MORGAN,  
Rockwell International Science Center,  
P.O. Box 1085,  
Thousand Oaks,  
CA 91360,  
USA

### *Authors' reply to 'Comments on "Effect of the starting $Al_2O_3$ and of the method of preparation on the characteristics of Li-stabilized $\beta''-Al_2O_3$ ceramics"'*

In connection with our paper Dr Morgan [1] raises several issues. We should like to take this opportunity to clarify some of the views expressed in our article.

We feel that our approach towards the problem under consideration is correct despite the inevitable pitfalls which may be encountered.

Let us now turn to some specific points stressed by Dr Morgan.

It is by now certain that the structural state of the precursor  $Al_2O_3$  as well as the effect of specific additives such as Mg, Li and F are of decisive importance for the phase composition of the  $\beta$ -alumina phases formed during synthesis and sintering. In a previous paper [2] the reaction of  $\beta$ -alumina phase formation has been described as topotactic in the sense used by Dent Glasser *et al.* [3].

The phase formation process proceeds via a syntactic intergrowth between the hexagonal  $\beta-Al_2O_3$  and the rhombohedral  $\beta''-Al_2O_3$  phases which can cause disorder at a level of about 5.0 nm i.e., at a certain number of spinel blocks. However, in principle, the spinel blocks themselves are regularly arranged [4]. This does not preclude the existence of vacancies and point defects. This may be connected with the observation that as structural elements the spinel blocks are first formed at the lowest temperatures (appearance of the  $hk\bar{l}0$  reflections in the X-ray diffraction patterns) when synthesis is started from sulphates and

the powdered material passes through an amorphous state [5].

Of course, the case in which the precursor is  $\gamma-Al_2O_3$  or  $\alpha-\gamma-Al_2O_3$  is a more specific one since already existing spinel blocks are involved in the topochemical reaction. As already shown [2, 4] a drastic rearrangement of the structure is unnecessary for generating the  $\beta$ -alumina phases. However, under these conditions the stacking faults of the precursor  $\gamma-Al_2O_3$  are inherited by the  $\beta$ -alumina formed [2].

We think that the intensity ratios of characteristic diffraction peaks is the only way to assess the quantitative relationship between  $\beta$ - and  $\beta''-Al_2O_3$ . This has already been done by other authors [6, 7] using various peaks. We selected the  $20\bar{2}6$  and  $20\bar{2}7$  reflections of  $\beta-Al_2O_3$  and the  $02\bar{2}.10$  reflection of  $\beta''-Al_2O_3$  because they are well separated and their intensities can be accurately measured. Furthermore, in classical X-ray powder diffractometry it is improbable that syntactic intergrowths would significantly affect the intensity ratios, since the mode of preparation of the samples and the geometry of the instrument lead to an averaging of the intensities.

The conclusions drawn by different authors concerning the phase changes and interactions in the high-temperature range of existence of the  $\beta$ -alumina phases are sometimes conflicting but are based on the analysis of the system under equilibrium or quasi-equilibrium conditions. Naturally, at this high energy level, the process proceeds at a high rate and equilibrium can be achieved rapidly.

According to us and to the views expressed

by Morgan [4] the approach towards equilibrium of the  $\beta$ -alumina polytypes is determined by the possibility of ion exchange between the co-existing phases. At high temperatures the eutectic melt constitutes a favourable medium. But once formed and subsequently solidified, such a eutectic may also favour phase interactions at lower temperatures although at lower rates, e.g., the phase conversion of  $\beta$ - $\text{Al}_2\text{O}_3$  to  $\beta''$ - $\text{Al}_2\text{O}_3$  by post-sintering annealing at  $1400^\circ\text{C}$  [7].

In the low-temperature region (below  $1400^\circ\text{C}$ ) the achievement of equilibrium states is extremely complicated and sometimes even impossible and we would like to agree here with Morgan's opinion, in the sense that it is not known whether and to what extent such an equilibrium is reached, and that in addition, no sure conclusions can be drawn concerning the thermodynamic stability of a given phase.

Our experiments show that there are no changes in the X-ray diffraction patterns of Li-containing  $\beta$ -alumina powders after an additional 24 h thermal treatment at  $1350^\circ\text{C}$ . However, in our view, it is doubtful whether the local distribution of lithium in the structure of  $\beta$ -alumina in this case is the same as in that of a composition treated by liquid phase sintering.

The stabilization of the  $\beta$ - $\text{Al}_2\text{O}_3$  phase observed by us when the synthesis is performed in the presence of  $\text{Li}_2\text{O}$  may constitute a kinetic effect, i.e., a change in the rate of formation of this phase, and this result has a practical significance. The influence of the  $\text{Li}_2\text{O}$  added manifests itself only in the cases in which lithium is introduced as a soluble and thermally decomposable form, e.g.,  $\text{LiNO}_3$ .

If lithium is present as an insoluble and thermally stable compound, for instance  $\text{Li}_2\text{O} \cdot 5\text{Al}_2\text{O}_3$

( $\text{LiAl}_5\text{O}_8$ ) its influence is blocked and phase formation proceeds in the same way as if there was no lithium present. As a result the synthesized material contains a considerably smaller amount of  $\beta$ - $\text{Al}_2\text{O}_3$ .

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R. KVACHKOV  
A. YANAKIEV  
C. N. POULIEFF  
I. BALKANOV  
P. D. YANKULOV  
E. BUDEVSKI

Central Laboratory of Electrochemical  
Power Sources,  
Bulgarian Academy of Sciences,  
1040-Sofia,  
Bulgaria