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Ultrasonic homogenization of equivolumetric Al_2O_3/ZrO_2 suspensions

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The equivolumetric ZrO_2-Al_2O_3 ceramic composite shows very good mechanical properties due to its interpenetrating microstructure; unfortunately it is very difficult to achieve a well dispersed aggregates' free mixture. In this paper ultrasonication was used as a dispersion and mixing aid for aqueous suspension of ZrO_2-Al_2O_3 powders. The suspensions were stabilised using either an electrostatic or an electrosteric mechanism. The influence of ultrasonication time as well as solid contents in the suspensions were investigated via rheological measurements. The goal was to optimise the process in order to obtain a well dispersed system without aggregates. The results indicate that there is, for every system, a threshold time over which aggregates start to reappear.

1. Introduction

Zirconia has been used for many years to improve the mechanical properties of many ceramic matrices [1, 2]. In particular, in the system ZrO_2-Al_2O_3 the aforementioned oxide is usually in the range 5–15 vol.% and the outstanding mechanical properties of these composites is due not only to the transformation toughening effect of the zirconia but also to the grain growth control of the alumina obtained with the addition of a second-phase particles (zirconia).

Previous works [3, 4] had shown that an alternate method of inhibiting grain growth is to increase the amount of zirconia reaching the equivolumetric composition, developing in this way an interpenetrating microstructure in which the long-range interdiffusion is limited and therefore the growth of the individual phases is inhibited by virtue of the mutual topological constrain of the two phases.

Unfortunately as the second phase amount increases the possibility of developing clusters and/or agglomerates raises too. As a consequence differential shrinkage and therefore defects, at the interface between the two phases, are created (Fig. 1).

As a consequence of above, regardless the method used to produce the composite, the homogeneous distribution of the two phases is critical for the production of a fine grain microstructure and therefore improved mechanical properties. It is well known that the method by which the mixing-deagglomeration step is carried out is a critical issue in forming high quality green bodies and therefore reliable ceramic parts.

Colloidal processing which is composed of the dispersion of starting powders in liquid media and following consolidation is superior to conventional dry pressing in the control of density and microstructure of both green and sintered compacts [5, 6]. The main problem that can arise is the agglomerate formation inside the slurry (that obviously vanificate all the method's benefits) and/or a non well mixing of the phases, expecially when the second phase amount is high. For the ZrO_2-Al_2O_3 equimolecolar composition one suitable method of preparing the mix is to produce, with the two powders, two slurries in which agglomerates are broken by ultrasonic agitation to homogenise the powder suspension as well as the slurry.

Ultrasonication has been used extensively to disperse ceramic powders which are hard to disperse by other methods like ball-milling. Ultrasonic vibration induce pressure waves in the slurry which can generate cavities that can collapse violently producing intense stresses able to break powder agglomerates and homogenise the dispersion of the two components.

It has been shown that there is a small range in the power/time used, below this low limit the method is ineffective but above the upper limit the slurry properties are also degraded due to reagglomeration [7].

The present work has been undertaken in order to study and define the effects of time, being the power fixed, on an ZrO_2-Al_2O_3 equimolecolar composition. To assess the suspension behaviour a rheological characterisation has been carried out, being the rheological properties strongly dependent on the dispersion state [8, 9].

2. Experimental procedure

2.1. Materials

Three types of suspensions were investigated: (a) pure alumina, (b) pure zirconia, and (c) ZrO_2-Al_2O_3 equimolecolar composition. Alumina (Advanced Alumina AA-05 with $d_{50} = 0.46\,\mu$m from Sumitomo Chemical Co., Tokyo, Japan) and zirconia (3 mol.% stabilised zirconia PYT0, 5 with $d_{50} = 0.55\,\mu$m from

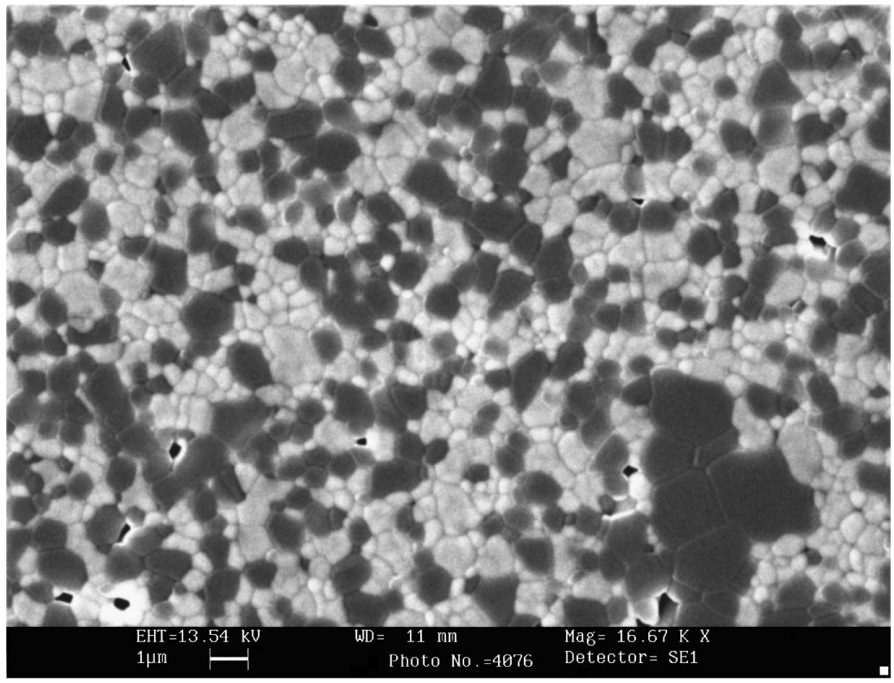


Figure 1 An example of Al_2O_3/ZrO_2 equivolumetric composite microstructure not well homogenised (via attrition milling). Aggregates and defects at interface between the two phases are evident.

Unitec Ceramics, U.K.) powders were used; the slurries were prepared by mixing together the powder with distilled water and either HNO_3 for pH adjustment in order to introduce a common surface charge on the particles and therefore an electrostatic stabilisation, or an organic dispersant (Reotan LA from Fratelli Lamberti, Italy) via electrosteric stabilisation achieved by adsorption of a polymeric additive which tail beyond the electric double layer thickness in such a way that overlapping of the polymer chains provides dominant repulsive forces. The pH range in which both alumina and zirconia powders are dispersed is from 2 to 3.5 [10], so we adjusted the pH around the value of 3. The solid content was either 20 or 30 vol.%.

Individual suspensions were mixed slowly using magnetic stirrer and after that each slurry was subjected to an ultrasonic agitation varying systematically the duration of this step. The ultrasonic apparatus consisted of a 20 kHz generator, a piezomectric trasducer and a probe with a titanium tip (model: XL2020, Heat System, USA). The power level was fixed at 120 W for the 20 vol.% and 150 W for the 30 vol.% slurries respectively. The ultrasonic horn was introduced directly in the centre of the slurries and to prevent overheating the sample containers were cooled in water-ice mixture.

2.2. Rheological characterisation

The efficiency of ultrasonic dispersion was estimated immediately after sonication, using small amount of each slurry. All rheological measurements were performed at 25 (±0,3) °C using a rotational viscometer HAAKE RV20 equipped with coaxial cylinder measuring system Money Ewart ME30 and measuring head CV100. The sample volume was 3 cc. The system's geometry is reported in Fig. 2a.

The rheological tests were carried out in an oscillatory flow regime, through the application of both constant frequency and strain (time-sweep) and constant strain with raising frequency (frequency-sweep) as summarised in Fig. 2b.

In dynamic measurements the strain is applied as a sinusoidal oscillation, as a function of the applied strain γ at a constant frequency ν (Hz) and the resultant stress in the material is recorded. The ratio between the amplitude σ_0 of the stress and the strain γ_0 is the absolute shear modulus $|G^*|$, therefore:

$$|G^*| = \frac{\sigma_0}{\gamma_0} \tag{1}$$

For a viscoelastic material there is a phase lag (δ) between the sinusoidal stress and strain ($0 < \delta < 90°$). From δ and $|G^*|$, the storage (G') and loss (G'') moduli can be calculate:

$$G = |G^*| \cos\delta \tag{2a}$$

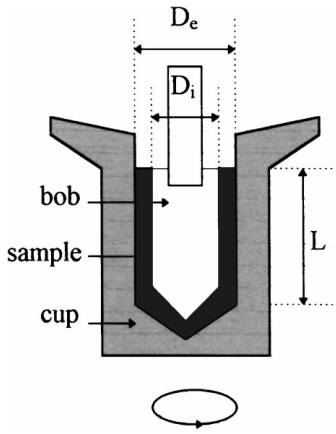
$$G' = |G^*| \sin\delta \tag{2b}$$

$$\tan\delta = \frac{G'}{G} \tag{2c}$$

$$G^* = G + iG' \tag{2d}$$

Following the procedure reported in Fig. 2 it was possible to assess (for each sample) as a function of the ultrasonication times, both the G^* modulus (time-sweep), that is the effects of loading; and the mechanical spectra (frequency-sweep), that is the viscous and elastic components (G' and G'') and therefore the stability of the suspension.

For highly structured systems, that is suspensions with flocced particles, the elastic component (G') is higher of the viscous one (G'') and both are slightly increasing with frequency. On the contrary, in stabilised suspensions, is the viscous component (G'') the higher (at lower frequencies), and both component strongly vary with frequency.



Internal Diameter D_i	[mm]	27.83
External Diameter D_e	[mm]	30
Length L	[mm]	24
Radii ratio R_e/R_i	[-]	1.078
Gap size	[mm]	1.08
Sample Volume	[cm^3]	3
Bob/Cup gap	[mm]	0.17

(a)

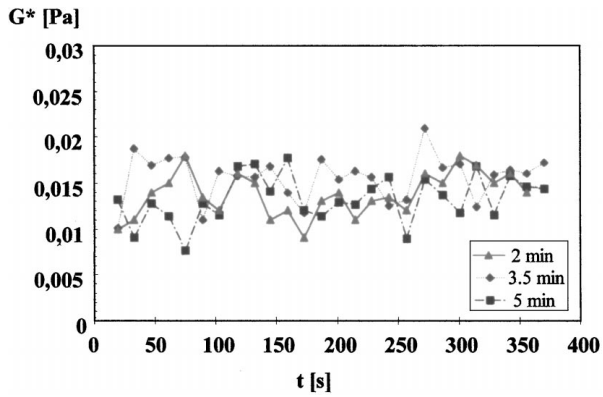
TEST	FREQUENCY [Hz]	STRAIN [%]	TIME [min]
time-sweep	1	5	6
frequency-sweep	0.0463-4.63	10	10

(b)

Figure 2 Rheological measurement conditions: a) system's geometry and b) test procedure.

3. Results and discussion

The results obtained during the rheological investigations illustrate either the relation between $|G^*|$ as a function of time (time-sweep) or as a function of frequency (frequency-sweep). As mentioned before the time-sweep tests will give an estimation of the loading effect on the suspension, therefore being $|G^*|$ the ratio between the maximum shear stress and the maximum



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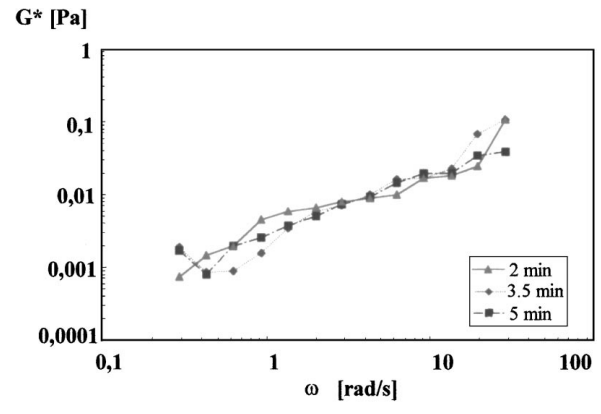
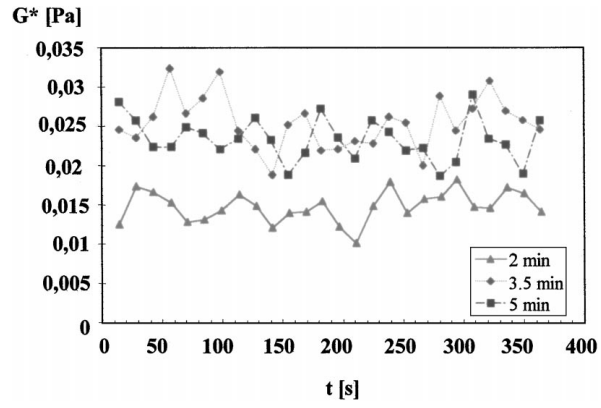


(b)

Figure 3 Rheological results for the Alumina suspension (20 vol%). a) Time-sweep test; b) frequency-sweep test. The legends report the ultrasonication times.



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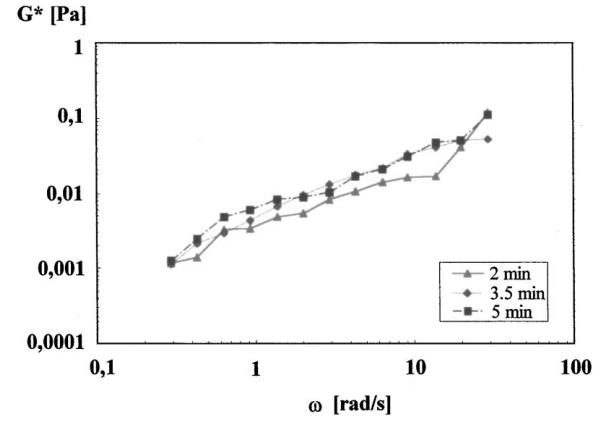


(b)

Figure 4 Rheological results for the Zirconia suspension (20 vol%). a) Time-sweep test; b) frequency-sweep test. The legends report the ultrasonication times.

strain (in our geometry it was fixed) the best suspension in terms of aggregates free will be that one with the lowest $|G^*|$.

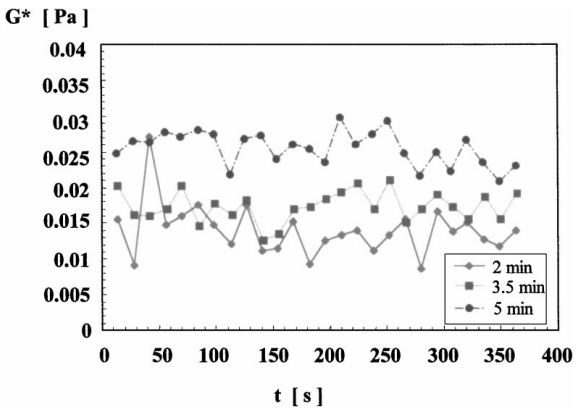
In Figs 3 and 4 the results for the alumina suspension (20 vol.%) stabilised with the organic dispersant and the zirconia (20 vol.%) stabilised in the same way are reported. It can be seen that, for the former suspension, there are no appreciable differences in $|G^*|$ increasing the ultrasonication from 2 to 5 min, however for the zirconia even though the behaviour is similar the best result is achieved with the shortest time (2 min.).

The results for the system ZrO_2-Al_2O_3 (20 vol%) also stabilised with the organic dispersant are reported in Fig. 5, following the previous results, the separate Al_2O_3 and ZrO_2 suspensions were ultrasonicated for 2 min. As seen there is a slight increasing of $|G^*|$ with ultrasonication time.

In Fig. 6 the results for the systems ZrO_2-Al_2O_3 (20 vol%) with Reotan or with a controlled pH, are reported, no differences can be noted between the two systems.

In Fig. 7 the results for the ultrasonication of the system ZrO_2-Al_2O_3 with 30 vol.% solid content are reported: in this case the $|G^*|$ values are always higher compared with the 20 vol.% suspension, decreasing with ultrasonication time, and no differences can be appreciate changing the time from 5 and 10 min.

Regarding the mechanical spectra of the complete 20 vol.% suspension with the optimal ultrasonication time, in Fig. 8 the trend of both G' and G'' vs. ω are



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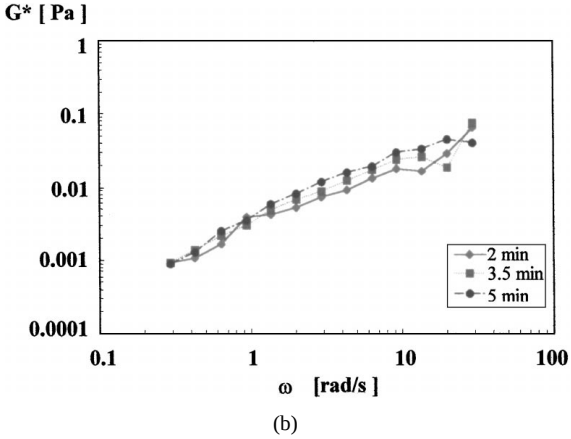
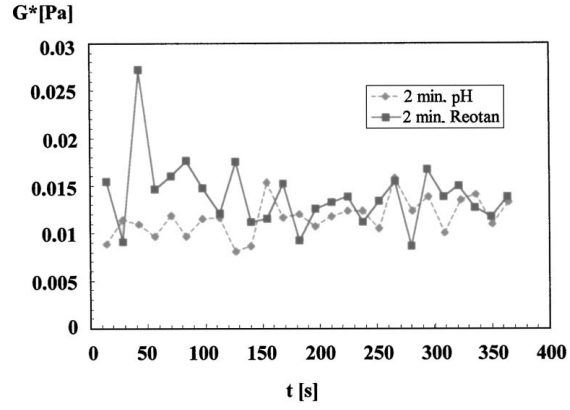


(b)

Figure 5 Rheological results for the 50Alumina-50Zirconia suspension (20 vol%). a) Time-sweep test; b) frequency-sweep test. The legends report the ultrasonication times.



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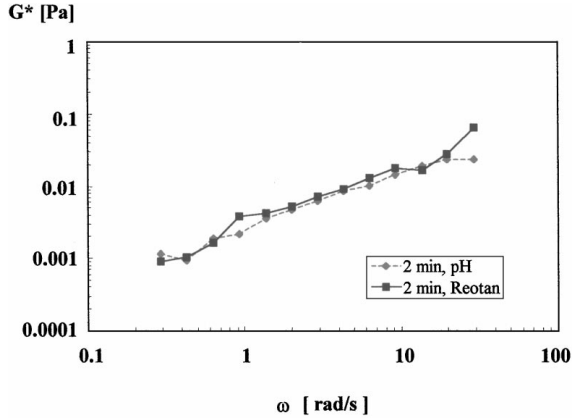
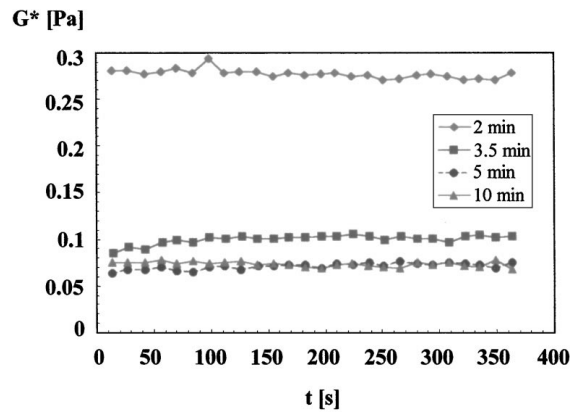


(b)

Figure 6 Rheological results for the 50Alumina-50Zirconia suspension with Reotan and pH control with same ultrasonication time of 2 min. a) Time-sweep test; b) frequency-sweep test.



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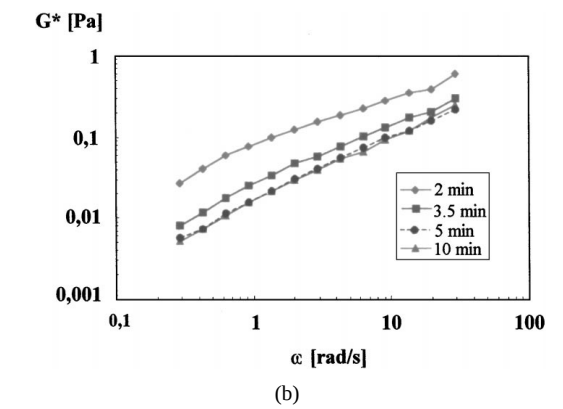

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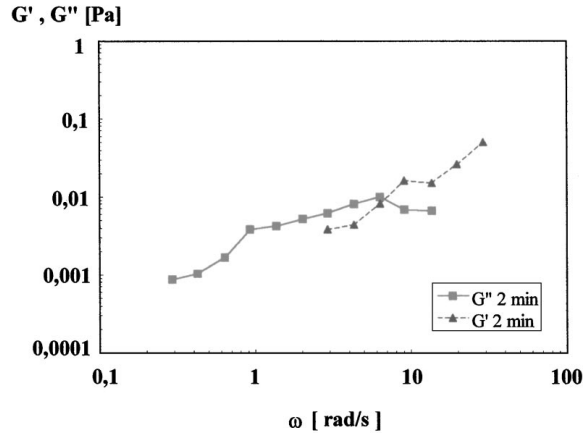
Figure 7 Rheological results for the 50Alumina-50Zirconia suspension (30 vol%) with four different ultrasonication times. a) Time-sweep test; b) frequency-sweep test. The legends report the ultrasonication times.



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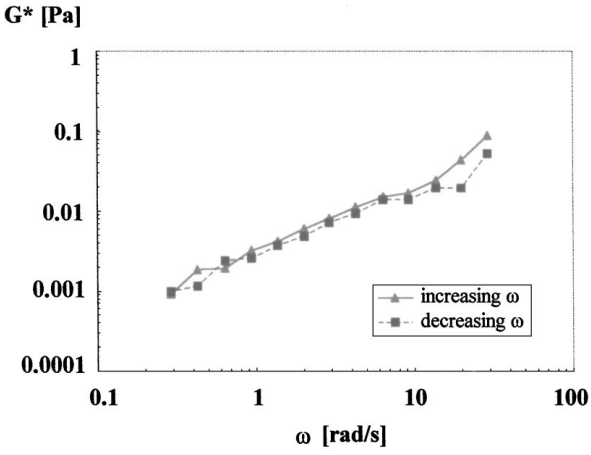

(b)

Figure 8 Results for the 50Alumina-50Zirconia suspension (20 vol%): a) G' and G'' vs. ω, the ultrasonication time was 2 min; b) G^* vs. ω for increasing and decreasing frequency.

plotted; the behaviour is typical of a well stabilised system.

4. Conclusions

The rheological characterisation of an equivolumetric ZrO_2-Al_2O_3 suspension (20 vol% of solid content) showed that the optimum ultrasonication time, regardless the dispersion method used (electrosteric or electrostatic), is already reached after 2 min. Increasing the solid content to 30 vol% the ultrasonication step must be longer, but always in the range 5–10 min.

In the suggested ranges the suspensions have a good dispersion and stability. Increasing the ultrasonication time, higher values of $|G^*|$ were obtained, indicating the formation of aggregates.

References

1. F. F. LANGE, *Journal of Materials Science* **17** (1982) 225.
2. A. G. EVANS and R. M. CANNON, *Acta Metallurgica*, **34**(5) (1986) 761.
3. J. D. FRENCH, M. P. HARMER, H. M. CHAN and G. A. MILLER, *J. Amer. Ceram. Soc.* **73**(8) (1990) 2508.
4. *Idem., ibid.* **75**(2) (1992) 418.
5. F. F. LANGE, *ibid.* **73**(1) (1989) 3.
6. A. BLEIER and C. G. WESTMORELAND, *ibid.* **74**(12) (1991) 3100.
7. M. AOKI, T. A. RING and J. S. HAGGERTY, *Advanced Ceramic Materials* **2**(3A) (1987) 209.
8. C. GALASSI, L. ESPOSITO, E. RASTELLI and E. RONCARI, *Third Euro-Ceramics* **1** (1993) 609.
9. C. GALASSI and R. LAPASIN, *Fourth Euro-Ceramics* **2** (1994) 15.
10. A. AKASAY, F. F. LANGE and B. I. DAVIS, *J. Amer. Ceram. Soc.* **66**(10) (1983) C190.

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