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Defect strategies for an improved optical quality of transparent ceramics

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ABSTRACT

For the past years most reports on transparent ceramics were focused on improvements of primary parameters like total and in-line transmission, scattering and absorption losses. The present paper directs the attention to previously neglected issues such as the quantified representation of remaining visible defects and the diversity of optical quality criteria for different groups of applications.

1. Introduction

As in other fields of science and technology most publications about transparent ceramics give an impression of steady progress: Authors are in a competition for highest transmittance, frequently illustrated by nice photos of (commonly small) samples, and on conferences as the annual Laser Ceramics Symposium most sophisticated lasing additives *to* the transparent ceramic (e.g. a garnet) are cultivated with an emphasis which makes believe that any question about the optical quality *of the garnet host* have been solved by a majority of authors long ago. In parallel, we observe an inflationary use of terms like "optoceramic" even for ceramics with modest transparency or in papers and patent applications which do not care about property criteria for real optical products. A complex site on Wikipedia about "Transparent Ceramics" [1] gives an example when in Section 5.2 Spinel the statement

> «Magnesium aluminate spinel ($MgAl_2O_4$) is a transparent ceramic … with an excellent optical transmission … in its *polycrystalline* form. *Optical quality* transparent spinel has been produced by …»

is followed by two references from 1970 and 2000 – suggesting, thus, that *polycrystalline* transparent spinel ceramics with "*optical quality*" were known since that time. Which is, of course, not the case: A search for the two references reveals that the elder one is a patent which describes the growth of spinel *single crystals*, and the later reference is about transparent *armor* – with the modest request of a transparency like common car windows.

In fact, it is quite difficult to find information about relevant quality parameters and their critical values a ceramic will have to match as a promising candidate for "optical" uses. On the other hand, even without specified knowledge most people know that glass for optical lenses and glass for apartment windows are quite different materials and need different manufacturing technologies associated with very different costs. It is, therefore, evident that common transparent ceramics must not be addressed as optoceramics. The quality issue is, however, only apparently easier for products as safety windows with the one "optical" request that we want to look through. For this latter group it is the fracture mechanical background which makes us wonder why flaws are so rarely addressed: Independent of different critical stress intensity values K_{Ic}, non-cubic ceramics as corundum (α-Al_2O_3) [2] or tetragonal zirconia (ZrO_2) [3] are manufactured with strength values $\geqslant$400 and frequently >600 MPa associated with relatively *small* flaws. However, these ceramics cannot be manufactured with high in-line transmission because of birefringent scattering effects [4]: High transparency needs optically isotropic (i.e. cubic) crystals. Unfortunately, the practical experience of the past 40 years shows that cubic ceramics are not among the strongest and toughest ceramics. Even after pressure-assisted sintering their strength is limited indicating larger flaws which *should be visible* in transparent grades. For example, cubic spinel ($MgO{\cdot}nAl_2O_3$) is one of the most thoroughly investigated transparent ceramics, and best grades exhibit a 4-point bending strength of 200–300 MPa associated with a K_{Ic} of about 1.7–2 MPam (measured e.g. by single-edge V-shape notched beams with a notch width at the tip $\leqslant$0.02 mm) [5,6]. Fracture of polished transparent polycrystals is governed by inner flaws of the microstructure (e.g. small residual pores) and not by surface scratches as it is typical for ground ceramics or

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amorphous glass products. The effect of a penny-shape crack with diameter d on the strength σ_f is described by

$$\sigma_f = \sqrt{(\pi/2)K_{IC}/\sqrt{d}} \quad (1)$$

and gives, with the typical strength and toughness data of "best" spinel grades an average flaw size of about 50–150 μm. Spherical pores are less critical for the strength than sharp cracks, but real sintered ceramic microstructures rather exhibit incompletely sintered *porous areas* with a stress intensity ratio that can be higher than that of a penny crack. As a rough approach, Baratta [7,8] established expressions for the case of peripherally cracked spherical voids (with diameter d_p) which for long crack lengths $L \gg d_p$ converge with Eq. (1) but give

$$\sigma_f = 0.35K_{IC}/\sqrt{d_p} \quad (2)$$

for short cracks ($L \ll d_p$) approximating the situation of a spherical porous space with a small peripheral flaw. For transparent spinel ceramics Eq. (2) gives critical flaw sizes of about 15–35 μm. The reality may be somewhere intermediate between the flaw size estimates of the two equations stretching over defects from about 20 up to 100 μm. These estimates enforce some important conclusions:

(1) Based on *average* 4-point bending strength and K_{Ic} data we are *not* talking about *few* largest flaws which initiate fracture. Instead, we have to expect defect *populations* with sizes of e.g. 20–100 μm which are more or less homogeneously distributed throughout the transparent microstructures.
(2) In a *transparent* ceramic material, most of these defects will be *visible* by careful visual inspection and may deteriorate the optical performance depending on given specifications.
(3) Voids >1 μm may initiate scattering losses for longer infrared wave lengths but should not significantly deteriorate the *visible* in-line transmission (cp. e.g. the dependence of scattering losses on pore size and refractive index given by Fig. 1a in ref. [9]). Some scattering with negative impact on the visible transparency is, however, possible when fracture is not initiated by individual larger pores but by incompletely sintered *porous areas* composed of a multitude of *small* pores <1 μm.

Based on these considerations, the present report is aimed at contributing to the following questions:

- Which experimental shortcomings are responsible for the only minor attention to visible defects in most publications, and which photographic approaches can provide the requested evidence?
- Which different optical quality criteria have to be observed for such different targets as transparent ceramics for safety windows, for special optical uses, or for lasers?
- To which extent today's raw powders and manufacturing technologies match these quality criteria - and which are, eventually, fundamentally basic questions that have to be addressed yet?

2. Materials and methods

Surface and edge effects will affect the formation of "defects" the more the smaller the sintered samples are. With the frequently investigated thin and inch-size small discs it is, therefore, difficult to obtain reliable information about correlations between an observed flaw population and manufacturing parameters (as e.g. properties of raw powders, processing and sintering approaches). Thus, samples with thicknesses up to 20 mm and with lateral dimensions between 50 and 300 mm were preferred for the present investigations.

A reproducible manufacture of such larger ceramic samples needs powders which are available with sufficient amounts and with constant quality. Even for spinel as one of the most common transparent ceramics there is a limited number of commercial providers which match these requirements. Table 1 gives the most important parameters of the raw materials of the present investigation. Meanwhile Nanocerox has stopped the manufacture of spinel powder, probably because of the extreme costs of this synthesis.

The transparent spinel samples for the present study were prepared by the following steps:

- Aqueous processing started with careful powder deagglomeration by ultrasonification and milling.
- The study compared two options of low-defect shaping of the green bodies: (i) freeze-drying and granulation followed by uniaxial pre-pressing and cold-isostatic pressing (CIP) [10], (ii) gelcasting [2]. The comparison of these two approaches is most teaching because *pressing* is preferred by the industry but suffers a shortcoming which is critical for making *transparent* grades: Even when soft granules are completely destroyed during pressing, the external pressure will never arrive at any individual powder particle in a way that it is shifted to an optimum symmetrical position between all neighbors. As a consequence, an inhomogeneous arrangement of particles will give rise to inhomogeneous neck-formation, locally inhomogeneous shrinkage and, finally, difficult elimination of last pores. Successful *gelcasting*, on the other hand, associates a minimum viscosity of the slurry with maximum solid loading and provides full freedom for all particles to form a most homogeneous coordination by self-organization [11]. Slurry consolidation by polymerization fixes, then, this homogenous particle arrangement with minimum drying shrinkage and enables best conditions for a locally homogeneous sintering densification.
- All samples were pre-sintered in air up to complete closure of all open porosity followed by hot-isostatic post densification (HIP) in argon.

Table 1
$MgAl_2O_4$ spinel raw powders for the manufacture of transparent ceramics in the present investigation.

Manufacturer, grade	Synthesis	Purity	Specific surface (BET) (m^2/g)	Equivalent[a] particle size (from BET) (nm)	Costs[b] relative to α-Al_2O_3 with 150 nm particle size, purity 99.995%
Nanocerox (USA)	Flame spray pyrolysis	~99.995% ([Fe] ~ 20 ppm)	29–34	~53	~3000%
Baikowski Chimie (France), S30CR	Thermal decomposition of alum salts	~99.995% ([Fe] ~ 10 ppm)	28–31	~57	~150%
Taimei Chemicals (Japan), TSP-20	Thermal decomposition of ammonium carbonates	~99.995% ([Fe] ~ 1–6 ppm)	13–15	~120	~300%

[a] Equivalent spherical particle size D_{BET} calculated from specific surface area S by $D_{BET} = 6/(S \cdot \rho)$ assuming a density $\rho = 3.58$ g/cm^3.
[b] Costs for laboratory batches (5–20 kg).