Transparent Alumina: A Light Scattering Model

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Abstract

A model based on Rayleigh-Gans-Debye light scattering theory has been developed to describe the light transmission properties of fine-grained, fully dense polycrystalline ceramics consisting of birefringent crystals. This model extends light transmission models based on geometrical optics, which are only valid for coarse-grained microstructures, to smaller crystal sizes. We verify our model by measuring the light transmission properties of fully dense (>99.99%) polycrystalline alpha-alumina (PCA) with mean crystal sizes ranging from 60 μm down to 0.3 μm. The remarkable transparency exhibited by PCA samples with small crystal sizes (< 2 μm) is very well explained by this model.

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I. Introduction

Translucent polycrystalline alumina (PCA) is used as light transmitting material at high temperatures and in corrosive environments, e.g. in high pressure sodium lamps. Conventional translucent PCA is characterized by a very low porosity (< 0.1 %) and a relatively large mean crystal (or grain) size (15 - 30 μm). This material has a high diffuse forward transmission but only a low in-line transmission so that it is translucent rather than transparent, as is demonstrated in figure 1 and figure 2.

In the literature\textsuperscript{1,2} many possible reasons for the translucency of conventional PCA can be found such as: the scattering of light at grain boundaries, at pores, at second phase inclusions, and at rough surfaces. This is schematically illustrated in figure 3. Obviously, light scattering at rough surfaces can be avoided by a proper preparation or by polishing the surfaces. Furthermore, there are practically no inclusions (second phase particles) present in high-purity PCA. Therefore, grain boundaries and pores remain most important for the light scattering of high-purity PCA.

While it is clear that a low porosity is a prerequisite for a high transmission in order to minimize light scattering at pores, completely different ideas about the role of the grain boundaries can be found in the literature. Mostly it is thought that the grain boundaries cause a certain degree of light scattering due to the birefringence of alumina\textsuperscript{1,3,4,5}. Note that polycrystalline materials with a cubic crystal structure (no birefringence) like Y\textsubscript{2}O\textsubscript{3} or Y\textsubscript{3}Al\textsubscript{5}O\textsubscript{12} (YAG) can indeed be perfectly transparent when processed properly\textsuperscript{6,7,8}. This means that the light transmission of PCA should improve with increasing grain size because a larger grain size implies less grain boundaries. On the other hand, it was discovered that the in-line transmission of PCA is significantly increased at small mean grain sizes (1 - 2 μm)\textsuperscript{2,9,10}. Even transparency was reported\textsuperscript{2,11}. It was concluded by Peelen\textsuperscript{9,10} that light scattering at grain boundaries can be neglected, in spite of the fact that grain sizes of 1 - 2 μm are still
significantly larger than the wavelength of light. The measured in-line transmissions by Peelen et al. were in good agreement with their calculations, which were solely based on the light scattering at residual pores. They suggested that even the densest large-grained samples still contain so many pores that every light beam hits at least one pore. The transparency of the fine-grained PCA was explained by a much smaller pore size so that many light beams are able to pass the sample without hitting a pore.

In contrast to this, Hayashi\textsuperscript{2} excluded the scattering of light at pores in their samples because of their high density. Furthermore, they found no pores by TEM. However, in spite of their very detailed investigations, they were not able to identify the origin of the light scattering in their samples.

The aim of this paper is to clarify the discrepancies that follow from the literature. In particular, the observed transparency of fine-grained PCA will be quantitatively explained by a model based on classical light scattering theory. The model will be tested with extremely fine-grained PCA samples.

The outline of this paper is as follows. In section two the experimental details are given. Section three contains the theoretical part where a model based on geometrical optics is introduced as a means to quantitatively explain the translucency of coarse-grained materials. In the same section also the Rayleigh-Gans-Debye light scattering model is introduced. The results are collected in section four where the effect of the grain-size and its distribution, as well as the effect of residual porosity is discussed. We end with a summary and conclusions in section five.
II. Experimental Procedure

The large-grained samples were prepared by extrusion of an $\alpha$-alumina powder with a mean particle size of 500 nm. The powder was doped with 300 weight-ppm MgO. After calcinating at 1200 °C in air the samples were sintered at 1800 to 2000 °C for 4 hours in wet hydrogen. Depending on the sintering temperature, mean grain sizes from 15 to 62 $\mu$m were obtained.

The fine-grained samples were prepared by slip- or pressure-casting using an $\alpha$-alumina powder with a mean particle size of 150 nm. No MgO or any other dope was added to these samples. The colloidal suspensions used for casting were carefully de-agglomerated and stabilized in water using a dispersant like nitric acid. The samples were sintered at temperatures of 1150 to 1250 °C for 2 hours in order to obtain closed porosity, which is obtained at $> 95\%$ of the theoretical density. Finally, the samples were subjected to Hot Isostatic Pressing (HIP) at 1200 to 1400°C and 200 MPa for 2 hours in argon. Depending on the HIP temperature, mean grain sizes from 0.3 to 8 $\mu$m were obtained.

All samples are fully dense unless stated differently. All samples were ground to a thickness of 0.8 mm and polished carefully on both sides in order to eliminate surface scattering.

The mean grain size was determined with SEM using polished samples, which were thermally etched at a temperature of at least 20°C below the sintering temperature. The grain size was determined by counting the number of grains in a certain area. From the average area per grain an apparent grain size $g$ was obtained, approximating the grains as spheres. The average cross sectional surface of a sphere with diameter $G$ is $1/6\pi G^2$, yielding the relation between the true grain size $G$ and the apparent grain size $g$: $G = \frac{1}{2}\sqrt{6 \cdot g} \approx 1.225 \cdot g$.

The total forward transmission (TFT) of the samples was measured by a spectrophotometer equipped with an integrating sphere, see figure 4a. In a similar way the total reflectivity (TR) was measured (figure 4b). The so-called real in-line transmission (RIT) was measured by using a red laser (645 nm) and a detector as shown in figure 4c. Due to the large distance
between detector and sample practically only unscattered light is measured. All light that is scattered at an angle larger than 0.5° is not detected. Therefore the RIT is a good measure for the transparency. Note that this real in-line transmission is different from the in-line or linear transmission, which is often found in the literature. The “normal” in-line transmission is mostly measured with a standard spectrometer with a large aperture (up to 3 - 5°) so that besides the RIT a lot of scattered light is measured as well. Therefore a high in-line transmission doesn’t necessarily imply that the sample is transparent. The unique parameter that quantifies the transparency is the RIT and therefore in this paper RIT-data rather than in-line transmission data are given.

Scattering profiles were measured with a detector that could be in-plane rotated around the sample, up to a scattering angle of 60°. The illuminating light source was a halogen lamp with a filter in front of it. The wavelength distribution of the out coming light had a maximum at a wavelength of 550 nm. The angular resolution of the set-up was approximately 1°, which could be adjusted with a diaphragm in front of the detector.
III. Theory

(1) Sources of light scattering

The most important origins of light scattering in high purity PCA are (rough) surfaces, pores and the grain boundaries. This is illustrated in figure 3. Light scattering at second phases (inclusions) can be neglected in high purity PCA. From TEM studies it is known that the grain boundaries of high purity PCA are very clean. Even for MgO-doped PCA we found no significant effect of the MgO on the optical properties of PCA up to a MgO content of 300 ppm by weight. Absorption of light of high purity PCA is generally low when it is sintered properly and can be neglected too. When the sample surfaces are smooth, the diffuse scattering of light at the surfaces can also be neglected, only the specular reflection at the surfaces of approximately 14% has to be taken into account. The small contribution of pore scattering in our samples was concluded from the measured diffuse reflection (back-scattering) of the samples, which was maximally 5%. As we will show later, the diffuse reflection is a good measure for the porosity because only the pores and not the grain boundaries are able to back scatter light in high purity PCA. In this chapter we will only concentrate on light scattering at grain boundaries.

Due to the scattering of light at grain boundaries the real in-line transmission decreases exponentially with the sample thickness $d$:

$$RIT = (1 - R_s) \cdot \exp(-\gamma \cdot d).$$  
Eq. 1

$R_s$ describes the reflection losses at the two sample surfaces ($\sim 0.14$) at normal incidence:
\[ R_s = \frac{2R'}{1+R'} \quad \text{with} \quad R'=\left(\frac{n-1}{n+1}\right)^2, \quad \text{Eq. 2} \]

where \( n \) is the refractive index of PCA and where \( \gamma \) is the total scattering coefficient which is the sum of both grain boundary and pore scattering contributions:

\[ \gamma = \gamma_{gb} + \gamma_{pore}, \quad \text{Eq. 3} \]

We here assume that \( \gamma_{pore} \) can be set to zero because of the low porosity of our samples. We will come back to pore scattering later. The scattering coefficient is a measure for the extent of light scattering in a given sample. It does not contain information about the angular distribution of the scattered light intensity, further referred to as the scattering profile. Equation 1 defines the RIT as incident light minus all scattered light. Therefore the RIT is equal to the unscattered transmission, and is the only correct measure for the transparency of a sample. Note that the RIT is affected by material variables (via \( \gamma \) and \( R_s \)) as well as by the sample thickness.

(2) Grain boundary reflection

Due to its hexagonal crystal structure \( \alpha \)-alumina (corundum) is birefringent. This means that the refractive index is not equal for the different crystallographic directions. For example, at a wavelength of 600 nm the refractive index of alumina is 1.768 for the ordinary ray (polarization perpendicular to the c-axis) and 1.760 for the extraordinary ray (polarization parallel to the c-axis)\textsuperscript{12}. The refractive index difference of 0.008 is virtually independent of temperature and wavelength while the refractive indices themselves change slightly\textsuperscript{12}. The birefringence leads to a discontinuity \( \Delta n \) of the refractive index at the grain boundaries if the crystallographic orientations of the neighboring grains are not the same. As in normal PCA
the grains are randomly oriented, the discontinuity $\Delta n$ at a given grain boundary should range from zero to maximally 0.008. Therefore on average the light will be refracted as well as reflected at a grain boundary. However, the reflectivity of the grain boundaries is extremely low due to the small discontinuity $\Delta n$. The reflectivity for perpendicular incidence can be calculated by\textsuperscript{13}:

$$R_\perp = \frac{(n_1 - n_2)^2}{(n_1 + n_2)^2}$$  \hspace{1cm} \text{Eq. 4}

Here $n_1$ and $n_2$ are the refractive indices of the two neighboring grains, the discontinuity $\Delta n$ is $n_1 - n_2$. Of course, the light will not pass all grain boundaries perpendicularly so that Eq. 4 does not give the general answer. The exact reflectivity can be calculated by using Fresnel’s laws\textsuperscript{13}. From Eq. 4 it can be calculated that the reflectivity is maximally $5\times10^{-6}$, even for the largest discontinuity $\Delta n$ (0.008). By assuming that the light passes all grain boundaries at an angle of $90^\circ$, the total maximum reflectivity $R_{\text{max}}$ in a sample with $m$ grain boundaries is given by:

$$R_{\text{max}} \approx 1 - (1 - R_\perp)^m$$  \hspace{1cm} \text{Eq. 5}

In a typical large-grained PCA sample of 1 mm thickness and a mean grain size of 20 $\mu$m a light beam will pass approximately 50 grain boundaries. For this sample the total reflectivity is maximally $2.6\times10^{-4}$. Even for 1000 grain boundaries, the reflectivity is very low. Therefore it can be concluded that the reflection (back-scattering) of light at grain boundaries can be completely neglected in all PCA samples that are used in this study.
(3) **Grain boundary refraction**

In contrast to the reflection, the refraction of light at the grain boundaries cannot be neglected in PCA. First this will be shown qualitatively for large grains by simple geometrical optics. Geometrical optics can be applied when the grains are much larger than the wavelength of the light. (More exactly, the condition is $G \cdot \Delta n > 2 \pi \lambda_m$, when $G$ is the mean grain size and $\lambda_m$ the wavelength in the medium, see below.) The deviation of a light beam from its original direction can be calculated by Snell’s law\textsuperscript{13}:

$$n_1 \cdot \sin \alpha_1 = n_2 \cdot \sin \alpha_2$$  \hspace{1cm} \text{Eq. 6}$$

Here $n_1$ and $n_2$ are the refractive indices for the first and the second grain, respectively, $\alpha_1$ is the angle of incidence and $\alpha_2$ is the angle of the refracted ray of light. Both angles refer to the normal of the grain boundary surface. For an angle $\alpha_1$ of 45° and a discontinuity $\Delta n$ of 0.008 the deflection $\alpha_1 - \alpha_2$ of the light beam from its original direction results to 0.28°. This rough calculation shows that the refraction (deflection) of light at the grain boundaries cannot be neglected, especially when it is taken into account that a light beam has to pass tens or hundreds of grain boundaries in a typical PCA sample, depending on grain size and sample thickness.

The calculation of the light scattering profile for a real sample with many randomly oriented grain boundaries is quite difficult. The statistical distributions of the grain boundary orientations and of the refractive index discontinuities have to be taken into account, as well as multiple refraction. Such calculations that are based on geometrical optics were done by Dalisa et al.\textsuperscript{14} for polycrystalline ferroelectric ceramics, which are also birefringent. We adapted this geometrical model for PCA. We don’t give a detailed description of the
calculations, we will only show that this geometrical model cannot be applied for grain sizes smaller than \( \sim 20 \, \mu \text{m} \) for obvious reasons.

For a typical large-grained PCA sample of 1 mm thickness and a mean grain size of 40 \( \mu \text{m} \) the model gives a full width of half maximum (FWHM) of the scattering profile of about 4\(^\circ\). This value agrees reasonably well with the experiment, as is shown in figure 5. The FWHM of the scattering profile can be interpreted as a typical scattering angle and denotes how strongly the light is scattered during transmission.

Obviously this geometrical model predicts, at a given sample thickness, that the scattering profile should get broader with decreasing grain size because the light has to pass an increasing number of grain boundaries. Figure 5 however shows that the scattering profile is only weakly dependent on the grain size below 30 \( \mu \text{m} \). Furthermore, at grain sizes smaller than 3 \( \mu \text{m} \) the refraction of light scattering is so reduced that part of the light is transmitted without any scattering. Figure 6 shows two scattering profiles corresponding to a 20 micron grained sample and a 1 micron grained PCA sample. The sharp peak at small scattering angles is a clear demonstration of the suppressed light refraction. It indicates that this sample has become partially transparent. The suppressed light refraction at small grain sizes is in clear contradiction with the geometrical model.

(4) Grain boundary scattering: Raleigh-Gans-Debye theory

In order to understand the suppression of light refraction, we now apply Mie theory on the birefringent alumina crystals. Key to this approach is that we approximate the fully dense ceramic microstructure as nearly index-matched monodisperse spheres that are randomly distributed in a homogeneous matrix. The spheres have a radius \( r \) and a refractive index \( n_2 \)
whereas the matrix has a slightly different refractive index $n_1$ as is sketched in figure 7. The diameter $2r$ of the spheres equals the mean grain size $G$ of the PCA and the absolute refractive index difference $|\Delta n| = |n_2 - n_1|$ has to be smaller than $\Delta n_{\text{max}}$, which is 0.008. In principle $\Delta n$ should be equal to the birefringence averaged over all grain orientations, which means that for an isotropic distribution $\Delta n$ is equal to $2/3\Delta n_{\text{max}}$ which is equal to 0.0053. It will be shown that $\Delta n = 0.0050$ leads to an excellent agreement between the model and the experimental data. The refractive index $n_1$ of the matrix is set to 1.760 which is the mean refractive index of PCA.

Of course this model strongly simplifies the real microstructure because (i) both the orientation-dependent and polarisation-dependent refractive index of the grains (due to the birefringence) is approximated by a mean value, (ii) the distribution of grain sizes is approximated by the mean grain size, and (iii) the grain shape is approximated by spheres. Nevertheless the model contains all relevant physical parameters which allows an analytical analysis of the optical properties of a fully dense ceramic microstructure consisting of birefringent crystals.

As the random position of the crystals in the model does not lead to structural interference effects and the small refractive index difference leads to predominantly single scattering, the grain boundary scattering coefficient can be calculated by:

$$\gamma_{gb} = N \cdot C_{sca}. \quad \text{Eq. 7}$$

$N$ is the density of spheres (number/volume) in the model-sample. As the PCA is fully dense and 100% pure, the volume fraction of spheres is equal to $\frac{1}{2}$ which implies that:
\[ N = \frac{1}{2} \cdot \frac{1}{\frac{4}{3} \pi \cdot r^3}. \quad \text{Eq. 8} \]

\( C_{\text{sca}} \) in Eq. 7 is the scattering cross section of one single sphere. In principle, the scattering cross section can be calculated by applying Mie theory. This can only be done numerically. However when the phase shift that is caused by the scattering objects (grains) is small, an analytical approximation can be made which leads to the so-called Rayleigh-Gans-Debye scattering. In this limit the scattering cross section can be written as:

\[ C_{\text{sca}} = \frac{8\pi^3 r^4}{\lambda_m^2} \left( \frac{\Delta n}{n} \right)^2, \quad \text{Eq. 9} \]

where \( n \) is the (average) refractive index of alpha-alumina (1.76) and \( \lambda_m \) is the wavelength of the incident light in the medium. This approximation is valid when:

\[ 2 \cdot r \cdot \Delta n \ll 2\pi \cdot \lambda_m \quad \text{Eq. 10} \]

Here \( \lambda_m \) is the wavelength of the light in the medium (\( \lambda_m = \lambda_0 / n \)). This relation is fulfilled well for diameters (i.e. grain sizes) smaller than 10 \( \mu \)m and visible light in the case of alpha-alumina. Therefore the scattering cross section of the grains can be written as:

\[ \gamma_{gb} = 3 \cdot \frac{\pi^2 r}{\lambda_0^2} \cdot \Delta n^2 \quad \text{Eq. 11} \]

By combining equation 11 and equation 1 one finally arrives at:
\[ RIT = (1 - R_s) \exp \left( - \frac{3\pi^2 r \Delta n^2 d}{\lambda_0^2} \right) \]  
Eq. 12

With this equation the real in-line transmission can be calculated as a function of grain size, wavelength and sample thickness. This equation is in principle applicable to all birefringent polycrystalline materials as long as the restrictions bound to the derivation of the Rayleigh-Gans-Debye theory are fulfilled. The assumption that multiple scattering can be neglected can be checked by calculating the scattering length \( \gamma^{-1} \), which should be larger than the sample thickness \( d \). For a sample thickness of 1 mm this is a good assumption when the grains are smaller than 1 micron.

**IV. Results and Discussion**

(1) **Verification of the model**

To test the correctness of the model, RIT values of various samples with a thickness of 0.80 mm were measured using a red laser with a wavelength of 645 nm. The corresponding grain sizes were determined by SEM and the data are plotted in Figure 8. The samples had a diffuse reflectance smaller than 5% and therefore can be considered as essentially pore-free as will be discussed below. Together with the experimental data, equation 12 is plotted where \( \Delta n \) was used as a fitting parameter. Excellent agreement between the theoretical curve and the experimental data points is obtained for a value of \( \Delta n \) of 0.0050, which is very close to what is expected theoretically (0.0053). The highest RIT that is measured is 71%. As the RIT of sapphire of 86% corresponds to 100% transparency, the RIT of 71% corresponds to a transparency of 83% (at a sample thickness of 0.80 mm). To our knowledge such high real in-line transmissions of PCA have never been reported in the literature.
Another way of testing the model (as well as the material) is by measuring the RIT as a function of the wavelength of one given sample. Figure 9 shows the wavelength dependence of the RIT. As expected, at long wavelengths the RIT gradually approaches the theoretical value of 86% (only surface reflection losses) whereas the RIT goes down rapidly at smaller wavelengths. A small discrepancy between experiment and theory becomes noticeable especially at smaller wavelengths. The experimentally determined RIT values are slightly smaller than is given by the theoretical curve. Apparently there are more scattering losses in the sample than is accounted for by the model. This might be due to the approximation that all crystals are equally sized whereas in practice the grain size is not uniform. Also an extremely small amount of residual porosity of very small pores (<100 nm) may be responsible for the observed difference at small wavelengths.

The physical consistency of the model is verified by comparing the experimental scattering profiles of a sample with grains larger than 1 micron and of a sample with sub-micron grains. The curves are given in figure 10. Both curves exhibit a clear transparency peak, which, as is expected, for the sample with the smallest grains is higher than for the sample with an average grain size of 2 microns. A remarkable difference that is not immediately obvious is the convex shape of the scattering profile for the sample with an average grain size of 2 micron and the concave shape of the scattering profile of the 0.4 micron sample.

(2) Distribution of grain sizes

The theoretical scattering profiles are obtained by summation of the scattering profiles of all spheres that are present in the detected scattering volume. As the crystals in the sample have different sizes, the model should be adapted to a model consisting of polydisperse spheres. This allows the calculation of scattering profiles that come more close to the experimental
curves. In the Rayleigh-Gans-Debye limit the scattering profile of unpolarized light for one single sphere with refractive index $n$ and a radius $r$ is given by:

$$I(\beta) = I_0 \cdot \frac{32\pi^4 r^6}{9\lambda_m^4 l^2} \cdot \left( \frac{\Delta n}{n} \right)^2 \cdot (1 + \cos^2(\beta)) \cdot P(u),$$  \hspace{1cm} \text{Eq. 13a}

with $\lambda_m$ is the wavelength of the light in the medium, $l$ the distance between the sphere and the detector, $\beta$ the scattering angle, $\Delta n$ the refractive index difference between the sphere and the surrounding medium and with $P(u)$ the so-called form factor which for a sphere is given by\textsuperscript{16}:

$$P(u) \equiv \left[ \frac{3}{u^5} (\sin u - u \cos u) \right]^2$$  \hspace{1cm} \text{Eq. 13b}

where $u$ is:

$$u \equiv \frac{4\pi r}{\lambda_m} \cdot \sin \left( \frac{\beta}{2} \right)$$  \hspace{1cm} \text{Eq. 13c}

The total scattered intensity is the sum of all spheres present in the detected scattering volume $V$. For monodisperse spheres this gives rise to a factor $\rho \cdot V$ in front of equation 13a:

$$I_{total}(\beta) = \rho \cdot V \cdot I_0 \cdot \frac{32\pi^4 r^6}{9\lambda_m^4 l^2} \cdot \left( \frac{\Delta n}{n} \right)^2 \cdot (1 + \cos^2(\beta)) \cdot P(u).$$  \hspace{1cm} \text{Eq. 14}
where $\rho$ is the number density. $P(u)$ is drawn in figure 11 which reveals that $P(u)$ is an oscillating function with clear minima and maxima. The $(1+\cos^2(\beta))$ term, which stems from the fact that the light is unpolarized, is a monotonically descending function at forward scattering angles. Therefore the form factor determines the shape of the scattering profile. The location of the primary minimum of $P(u)$ is at $u = 4.5$. In order to incorporate the effect of polydispersity in a simple way, one should sum all different scattering contributions in the detected volume, which changes equation 14 into:

$$I_{total}(\beta) = I_0 \cdot \frac{32\pi^4}{9\lambda_m^4 r^2} \cdot \left( \frac{\Delta n}{n} \right)^2 (1 + \cos^2(\beta)) \sum_v r_i^6 \cdot P_i(u),$$  \hspace{1cm} \text{Eq. 15}$$

where the term

$$\sum_v r_i^6 \cdot P_i(u) = P_p(u),$$  \hspace{1cm} \text{Eq. 16}$$

is here referred to as the polydisperse form factor. For a system with a tri-modal and penta-modal distribution of spheres with equal numbers, the polydisperse form factor is calculated and plotted in figure 12. Due to polydispersity the clear minima and maxima of the form factor vanish and the shape gradually smoothens and becomes concave. For a sample with uniform grains of 0.4 micron, the first scattering minimum is located at an angle of about 80º (60º and $r=0.2$ micron is equivalent to $u \approx 3.5$). So for very small average grain sizes the primary minima of the summed form factors are located at large angles. The scattering profile between 0º and 60º of the sample with $G = 0.4$ micron is therefore determined by the convex shape of the form factor between $u = 0$ and $u = 4.5$. For a sample with a uniform grain size of 2 micron, the primary minimum is located at an angle of 15º (60º and $r=1$ micron is equivalent...
to u≈17.5). So for a sample with an average grain size of 2 micron, polydispersity leads to the concave shape of the scattering tail. It should be mentioned that for samples with an average grain size larger than 1 micron, multiple scattering cannot be neglected anymore. Rayleigh-Gans-Debye theory is in principle not applicable for these samples. However, the extent of multiple scattering seems to be only limited, as the experimental RIT data plotted in figure 8 collapse on the theoretical curve for G= 0.3 micron to G=8 micron.

(3) Porosity

Due to the high difference in the refractive index n between the gas-filled pores and the PCA (n_{pore} ~ 1, n_{PCA} ~ 1.76) pores can scatter light very effectively. The scattering coefficient γ for pore scattering is identical to equation 7 which expressed in terms of the total porosity p changes to:

$$\gamma_{pore} = \frac{p}{\frac{4}{3} \pi r_{pore}^3} C_{sca, pore}$$  \hspace{1cm} \text{Eq. 17}

C_{sca} in Eq. 17 is the scattering cross section of one single spherical pore. Equation 17 can only be used when all pores have the same radius r. Peelen et al. calculated the effect of porosity on the RIT\textsuperscript{10}. The pores are assumed to be randomly divided over a non-scattering homogeneous matrix with a refractive index of 1.76. Also here single scattering was assumed. The model presented in this paper closely resembles this representation. The Rayleigh-Gans-Debye approximation is however not legitimate for pores as the system is far from being refractive index matched (Δn=0.76). Therefore the scattering cross section of the pores must be calculated numerically by Mie scattering theory\textsuperscript{15,17}. The analysis given here is not directly applicable to porous polycrystalline materials as the scattering of the matrix (i.e. the crystals) is neglected in order to facilitate the calculations. The results of our Mie calculations, which
were obtained by using a dedicated computer program\(^{17}\), are summarized in figure 13. When the pore size decreases, the scattering cross section of the pores decreases very rapidly, which over-compensates the increase of the \(r^{-3}\) term in equation 17. On the other hand, when the pore size increases, the \(r^{-3}\) term over-compensates the increase of the scattering cross section. A minimum of the RIT exists when the pores are almost as large as the wavelength of the incident light. The effect of porosity on the RIT happens to be extremely strong: even at a porosity of only 0.1\% the RIT drops from 86\% to 1\% in this region of pore sizes. For a porosity of 0.01\% the RIT can be calculated via the relation:

\[
T(p_2) = (1 - R) \left( \frac{T(p_1)}{1 - R} \right)^{\frac{p_2}{p_1}}, \quad \text{Eq. 18}
\]

with \(T\) the transmission (either RIT or TFT). At 0.01\% porosity the RIT has decreased to 55\%, still a relative decrease of 35\%. The total forward transmission that is also given in figure 13 was calculated by integration of the calculated backward scattering profiles. Figure 13 clearly shows that the TFT, although less sensitive to porosity than the RIT, decreases due to porosity. The ratio between back- and total-scattering as a function of the pore diameter \(d\) is shown in figure 14, and reveals that this ratio strongly depends on the pore size. For small pores (diameter < 100 nm) the light scattering is almost isotropic (Rayleigh scattering): nearly 50\% of all scattered light is isotropically scattered backwards. For larger pores (diameter > 200 nm) the light is mainly scattered in forward direction. However, even for larger pores at least 5 \% of the scattered light is scattered backwards. These trends can also directly be concluded from figure 13 as one realizes that 86\% minus the TFT equals the total backward scattering, and the TFT minus the RIT equals the total forward scattering. The alumina samples with sub-micron grains were obtained by careful colloidal processing. The pores in these samples, if any, were always within the size range of 50-100 nm, say 75 nm on average.
At a porosity of 0.1% the back scattering amounts 22%. Such a high back scattering leads to a whitish rather than transparent appearance of the sample. But even at a porosity of only 0.01%, the back scattering is 2%.

From the analysis given above it follows that both RIT and total reflection (TR) are very sensitive to porosity. Even at an apparent density of 100% as measured by ordinary techniques like the Archimedes method, optical properties like the RIT and TR can identify residual porosity. In principle it is possible to calculate the porosity from these properties at a given average pore size and a narrow pore-size distribution. On the other hand it also follows that high transparencies of PCA can only be achieved by an accurate control over the grain size, as well as the porosity and the pore-size. The latter puts high demands on the colloidal processing of these materials.

V. Summary and Conclusions

The optical properties of coarse-grained fully dense translucent polycrystalline alumina samples were analyzed by using a model based on geometrical optics. Agreement with experiment was obtained for samples having an average grain size of 35 microns or larger. At grain sizes smaller than 35 micron this model fails to describe the optical properties of experimental samples and at grain sizes typically smaller than 5 microns the model completely breaks down as the samples become transparent. In this paper we give a quantitative explanation of the remarkable transparency of fine-grained alumina ceramics by applying classical Rayleigh-Gans-Debye light scattering theory. The ceramic microstructure is modeled as an almost index-matched system consisting of equally sized spheres that are randomly distributed in a homogeneous matrix. The model is applicable to any kind of optically anisotropic (i.e. birefringent) ceramic material if the anisotropy and the grain size is not too large. Fine-grained alumina samples were prepared by careful colloidal processing.
The samples exhibited real-in line transmissions up to 69% at a grain size of 300 nm and a thickness of 0.8 mm at a wavelength of 620 nm. The data were found to be in excellent agreement with the developed light scattering model. The shape of the scattering profiles can be explained qualitatively, by taking the size distribution of the grains into account. Although the experimental samples used in this study were fully dense, it is shown that residual porosity can have a pronounced effect on the transparency. This was demonstrated by Mie calculations which revealed that only 0.1% of residual porosity can completely deteriorate the transparency. Total reflection and real in-line transmission measurements are proposed as suitable techniques to access porosities, which are beyond the accuracy of currently used density measurements.

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Figures and figure captions

Figure 1: Translucent (left) and transparent (right) PCA. Both samples are 1 cm above the text. The mean grain size of the PCA samples 20 micron (left sample) and 0.5 micron (right sample). Both samples are 0.8 mm thick and polished on both sides.
Figure 2: Illustration of the light transmission of (a) large-grained PCA (translucent) with a high diffuse transmission and a low in-line transmission and (b) fine-grained PCA (transparent) with low diffuse transmission and a high in-line transmission.
Figure 3: Illustration of the most important light scattering mechanisms in PCA.
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Figure captions

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