Effect of pores on transmission properties of transparent ceramics

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Light scattering by the microstructure defects of transparent ceramics causes losses of light and has an effect on the transmission properties. Effects of pores on transmission were studied using the Mie theory. The in-line transmissions of transparent magnesium aluminate spinel were calculated as a function of wavelength, pore size, width of distribution and porosity. The results show that the in-line transmission gradually increases with an increase in wavelength. Porosity has great impact as the transmission decreases with the increasing of porosity. The minimum of the transmissions were observed when the pore size close to the optical wavelength. Furthermore, it should be noted that the in-line transmission increases with decreasing of the width in pore size distribution in the visible part of the spectrum.

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1. Introduction

Transparent ceramics have recently attracted appreciable attention of research due to their wide applications such as lasers [1-3], optical electronics [4] and transparent armor [5]. With the improvement of ceramic materials processing technology, many kinds of high-quality transparent polycrystalline ceramics have been developed, such as Al_2O_3 [6-7], $MgAl_2O_4$ [8-9], YAG [10], Si_3N_4 [11]. However, these polycrystalline ceramics did not exhibit the expected theoretical transmission, especially in the visible range. This situation has extremely limited the application of ceramics for optical and photonic applications. The optical behavior can be explained by the influence of the microstructural properties of ceramics.

Ceramic materials are formed from fine powders, yielding a fine grained polycrystalline microstructure. Optical transparency in ceramics is limited by the amount of light which is scattered and absorbed. The scattering centers in transparent ceramics include microstructure defects such as residual pores, second phase and grain boundaries. The grain boundaries do not decrease significantly transparency when the crystalline structure is cubic, and the presence of residual secondary phases could be avoided if the elaboration process is controlled.

The light scattering by residual pores strongly affects the light transmission of ceramics, because of the significant difference in the refractive index between the ceramics matrix and the pores. The pores between the grains can be eliminated with the grain boundaries migration. However, the pores entrapped inside the grains can be hardly eliminated even the pore size is very small. It has been shown that ceramics are opaque when the porosity is more than 1% [12-13]. Thus, scattering by residual pores is considered as the main cause of preventing the transparency of ceramics.

The pores are nanosized in the nano-ceramics, and the light scattering by pores decrease. It is thought that the effect of pores is only limited in nano-ceramics because the pore sizes are smaller than 100 nm [14-15], and some research has expanded the possibility nano-ceramics of developing with porosity more than 1% to obtain high transparency [16-17]. However, the existing experimental results can hardly give the quantitative analysis on the influence factors of pores, especially when the porosity is extremely low. The aim of the present work is to establish correlations between pore contents and optical properties of transparent ceramics in order to determine the porosity level leading to high transparency. We study the scattering by pores theoretically. A numerical model to calculate the transmission is present, and the impact of pore size, the width of distribution and porosity on the transmission is analyzed. In section 2, we describe the theoretical basis and the computational model in detail. In section 3, the calculated results of different parameters have been discussed. In section 4, we present our conclusions.

2. Theory and model

The scattering and absorbing of light by a homogeneous spherical particle can be treated by the classical Mie theory. According to this theory, the scattering light in any direction is described by two complex amplitude functions S_1 and S_2, where S_1 and S_2 are the vertical and horizontal components of the light [18].

$$S_1 = \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} (a_n \pi_n + b_n \tau_n) \tag{1}$$

$$S_2 = \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} (a_n \tau_n + b_n \pi_n) \tag{2}$$

Here, a_n and b_n are Mie coefficients, which can be expressed with the Riccati-Bessel function ζ_n and ψ_n.

$$a_n = \frac{\psi_n(\alpha)\psi_n'(m\alpha) - m\psi_n'(\alpha)\psi_n(m\alpha)}{\zeta_n(\alpha)\psi_n'(m\alpha) - m\zeta_n'(\alpha)\psi_n(m\alpha)} \tag{3}$$

$$b_n = \frac{m\psi_n(\alpha)\psi_n'(m\alpha) - \psi_n'(\alpha)\psi_n(m\alpha)}{m\zeta_n(\alpha)\psi_n'(m\alpha) - \zeta_n'(\alpha)\psi_n(m\alpha)} \tag{4}$$

where m is the relative refractive indices of the particle and the surrounding medium; $\alpha=2\pi r/\lambda$ is the corresponding size parameter, in which r is the radius of the spherical particle and λ is the wavelength of the incident light.

π_n and τ_n depend on the scattering angle θ, and can be expressed with the Legendre function $P_n^{(1)}$

$$\pi_n = \frac{P_n^{(1)}(\cos\theta)}{\sin\theta} \tag{5}$$

$$\tau_n = \frac{d}{d\theta} P_n^{(1)}(\cos\theta) \tag{6}$$

Thus, the extinction efficiency factor and the scattering efficiency factor of a spherical particle are expressed as [19]

$$Q_{ext} = \frac{2}{\alpha^2} \mathrm{Re}[\sum_{n=1}^{\infty} (2n+1)(a_n + b_n)] \tag{7}$$

$$\begin{aligned} Q_{sca} &= \frac{1}{\alpha^2} \int_0^{\pi} [|S_1(\theta)|^2 + |S_2(\theta)|^2] \sin\theta d\theta \\ &= \frac{2}{\alpha^2} \sum_{n=1}^{\infty} (2n+1)(|a_n|^2 + |b_n|^2) \end{aligned} \tag{8}$$

For a ceramic sample of thickness t, the in-line transmission can be expressed by the Lambert-Beer equation

$$T = (1-R) \cdot \exp(-\gamma_{ext} \cdot t) \tag{9}$$

Here, R is the total reflection loss which is dependent on the refractive index n of the ceramic

$$R = \frac{2R'}{1+R'} \quad , \quad R' = \left(\frac{n-1}{n+1} \right)^2 \tag{10}$$

The extinction coefficient γ_{ext} describes total light losses

$$\gamma_{ext} = \gamma_{abs} + \gamma_{sca} \tag{11}$$

where γ_{abs} is the intrinsic absorption coefficient; and γ_{sca} is scattering coefficient caused by the ceramic microstructure such as pores, grain boundaries and second phase particles.

In our study, the residual pores are considered as scattering particles and the light absorption is negligible in the wavelength range 400-5000 nm, so we have $\gamma_{ext} = \gamma_{sca}$. Because the porosity of tranparent ceramic is very low, the scattering by pores can be considered as incoherent single scattering [20].

Assuming a unique pore size, the scattering coefficient for N pores with radius r can be calculated as follow

$$\gamma_{pore} = NQ_{sca}\pi r^2 = \frac{3V_p}{4r} Q_{sca} \tag{12}$$

where V_p is the porosity.

In actual transparent ceramic, the grains have various sizes and there is always a spread in pore size. Here we assume that the pore volume within a logarithmic diameter which is distributed like a logarithmic normal distribution, as is mostly the case [21]:

$$f(r) = \frac{1}{\sqrt{2\pi} \cdot \sigma} \exp\left[-\frac{1}{2} \left(\frac{\ln r - \ln r_{av}}{\sigma} \right)^2 \right] \tag{13}$$

where r_{av} is the mean pore radius and σ is standard deviation.

The equivalent radius of pores defined by

$$r_e = \frac{\int_0^\infty f(r) r^3 dr}{\int_0^\infty f(r) r^2 dr} \tag{14}$$

Thus, the scattering coefficient of inhomogeneous pores can be expressed as

$$\gamma_{pore} = \frac{3V_p}{4r_e} \cdot \frac{\int_0^\infty Q_{sca}(r) f(r) r^2 dr}{\int_0^\infty f(r) r^2 dr} \tag{15}$$

3. Results and discussion

We take transparent magnesium aluminate spinel $MgAl_2O_4$ as the sample (thickness 1 mm). The refractive index of pore is set to 1, and the relative refractive indices $m=1/n$, where the refractive index of spinel sample can be written in terms of a Snellmerier model [22]

$$n = \sqrt{1 + \frac{1.8938\lambda^2}{\lambda^2 - 0.09942^2} + \frac{3.0755\lambda^2}{\lambda^2 - 15.826^2}} \tag{16}$$

The wavelength dependence of the in-line transmission is shown in Fig. 1. We can see that the transmission gradually increase with increasing wavelength. It should be noted that the value of transmission for a ceramic sample is affected by pore size and porosity. The sample can have high transmission in the visible part of spectrum with very small pore size and very low porosity, which we will discuss as below.

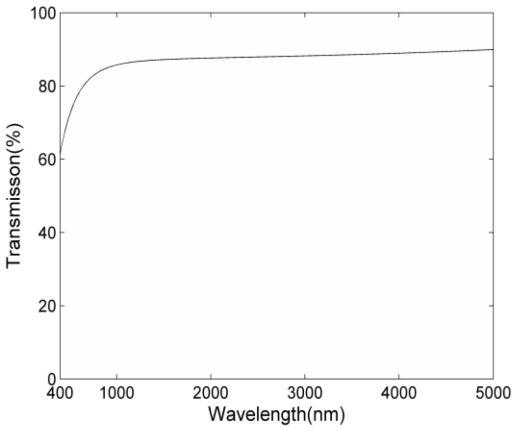

Fig. 1. Calculated in-line transmission as a function of wavelength; pore radius r=50 nm, porosity V_p=0.01%.

In Fig. 2, the transmissions as a function of porosity are shown for three different values of the pore radius r=1, 10 and 100 nm. The effects of porosity on transmission can be ignored when the pore radius is extremely small, because no reduction in transmission was observed with r=1 nm. For r=10 and 100 nm, transmission decreased with increasing porosity. Furthermore, there is obvious decrease when the pore radius is larger. For r=100 nm, the transmission decreased from 54% to 0.8% with the porosity increased from 0.01% to 0.1%.

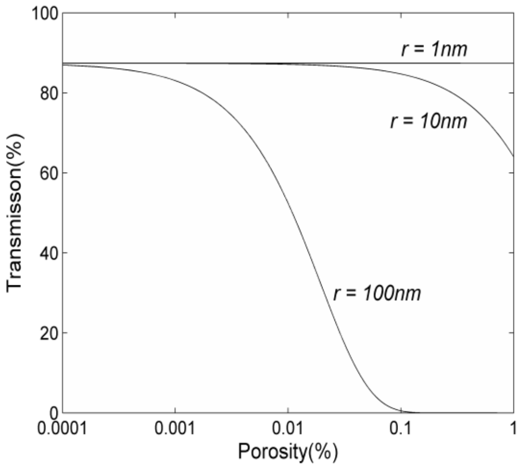

Fig. 2. Calculated in-line transmission as a function of porosity for three pore radius; wavelength λ=500nm.

For analyzing the effects of pore size on transmission, the transmissions as a function of the ratio between pore diameter and wavelength are shown in Fig. 3. For three different wavelengths λ=500, 2000 and 5000 nm, the transmissions increase in smaller pore regions because the scattering efficiency factor of pores decreases very rapidly, which overcompensates the increase of the r^{-1} term in equation (12). The minimum of the transmissions are observed at the ratio regions d/λ=0.7-0.8, in which the pore sizes are comparable with the wavelength of the incident light. This expectation is in accordance with the published experiment result [15].

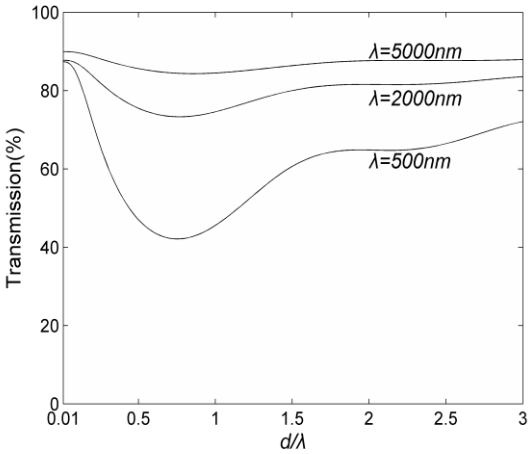

Fig. 3. Effect of pore size on in-line transmission at three different wavelengths, porosity V_p=0.01%.

The effect of pore size distribution on the in-line transmission in the visible part of spectrum is shown in Fig. 4. We assuming a lognormal pore size distribution with a mean pore radius r_{av} =50 nm and different standard deviation, and the range of the pore sizes is 10 nm to 100 nm. It is obvious that, the width of the distribution increases with increasing σ values, while the in-line transmission decreases in the visible part of the spectrum. The effect of pore size distribution on the in-line transmission at longer wavelengths can be ignored because the scattering in this range is very small. For further quantitative calculations, the measurement of small pores is necessary to estimate the size distribution.

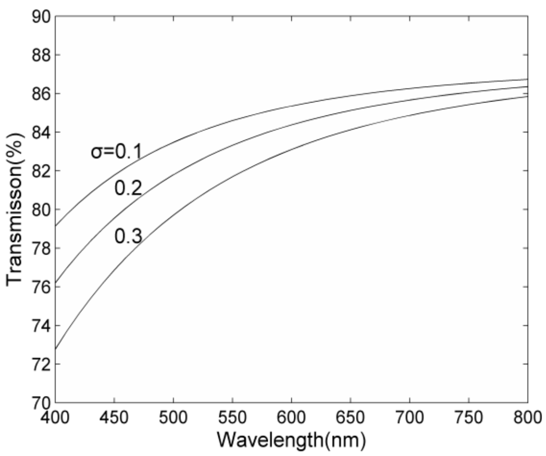

Fig. 4. Calculated in-line transmission with a lognormal pore size distribution as a function of wavelength; the mean pore radius r_{av} =50nm, porosity V_p=0.01%.

4. Conclusions

The light transmission of polycrystalline transparent ceramics was studied in terms of scattering by residual pores. The Mie theory was applied to calculate the scattering coefficients using different parameters. The results show that the in-line transmission is high in the near infrared region with a rapid decrease as the wavelength becomes smaller. Porosity has great impact as the transmission decreases rapidly with increasing porosity. The transmission increases in smaller pore regions and the minimum of the transmissions were observed when the pore size is close to the optical wavelength. We can conclude that the elimination of residual pores and the preparation of grains with uniform size are essential to improve transparency of ceramics.

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