Available online at www.sciencedirect.com
SciVerse ScienceDirect
Scripta Materialia 69 (2013) 149–154
Scripta MATERIALIA
www.elsevier.com/locate/scriptamat

Viewpoint Paper

Transmitting, emitting and controlling light: Processing of transparent ceramics using current-activated pressure-assisted densification

Y. Kodera, C.L. Hardin and J.E. Garay*

Advanced Materials Processing and Synthesis (AMPS) Lab, Materials Science and Engineering Program, Department of Mechanical Engineering, University of California, Riverside, CA, USA

Abstract—We review recent advances in using current-activated pressure-assisted densification (CAPAD) for fabricating polycrystalline ceramics that are transparent to visible and infrared light. In addition, we discuss important one-dimensional (vacancies), two-dimensional (grain boundaries) and three-dimensional (pores) defects that can affect optical properties. We pay special attention to procedures whereby the benefits of CAPAD can be used to ensure the precise control of microstructure that facilitates transparency and other functionalities.

Keywords: Spark plasma sintering (SPS); Field-activated sintering technique (FAST); Optical ceramics; Luminescent materials

1. Introduction

Transparent polycrystalline ceramics are becoming increasingly important in optical applications. The lure is that they can be larger and can be produced potentially more efficiently than traditional single crystals. In addition, when doping for functionalities such as photoluminescence, polycrystalline ceramics can have more uniform dopant distribution than single crystals pulled from a melt. A serious potential drawback to ceramics for optical applications is reduced optical quality caused by pores and other defects. However, researchers have identified processing routes to minimize defects leading to very high-quality optical ceramics such as sintered neodymium-doped yttrium aluminum garnet (Nd:YAG) that is now available commercially. These Nd:YAG ceramics are fabricated using pressureless sintering and now compete with single crystals for use as laser gain media.

An alternative to free sintering is current-activated pressure-assisted densification (CAPAD), which has been used for about a decade to produce transparent ceramics. CAPAD takes advantage of both high applied currents and mechanical pressure to deliver significantly higher densification rates than sintering or hot pressing [1]. CAPAD offers several advantages over traditional sintering techniques for producing transparent ceramics. First, fast processing kinetics facilitate the retention of fine grain and pore sizes, which in turn increases transparency. Secondly, the potential for non-equilibrium processing can lead to higher doping levels than would be possible using an equilibrium-constrained technique. Thirdly, excellent control of processing parameters such as high heating/cooling rates allow the targeting of "processing windows" that lead to sufficient density without causing detrimental effects such as phase changes.

Here we discuss some important microstructural features that determine visible and near-infrared (IR) optical properties in ceramics. We also discuss the above-mentioned benefits using examples from recent progress in the production of three classes of transparent ceramics: (i) passive ceramics whose primary application is transmitting light; (ii) photoluminescent ceramics that can emit light for applications such as solid-state lighting and lasers; and (iii) magneto-optical ceramics whose optical properties can be controlled using an externally applied magnetic field and can consequently be used for light manipulation in applications such as optical switches and diodes.

---

* Corresponding author. Tel.: +1 951 827 2449; e-mail: jegaray@engr.ucr.edu

1359-6462/$ - see front matter © 2013 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.scriptamat.2013.02.013

2. Role of microstructure on optical properties

It is well known that the microstructure of ceramics plays an integral role in optical properties. Important microstructural features and their interaction with light are schematically depicted in Figure 1. In materials with optical properties with cubic symmetry the refractive index *n* is the same in all directions, i.e. it is isotropic. In this case, the dominant microstructural feature is porosity. Each pore represents a significant change in refractive index from the ceramic material, causing reflection and refraction. However, a pore's scattering efficiency depends on its size. Figure 1a and b schematically shows the influence of a pore's length scale on light scattering. In materials with pore sizes in the micrometer range (dimensions comparable to the wavelength of the light) pores efficiently scatter light. In order to have high transparency in ceramics with pore sizes in this range, the porosity must be kept to a minimum, usually significantly less than 1%. On the other hand, when the pore sizes are in the nanometer range (<100 nm) their interaction with visible light becomes minimal and the optical transparency increases (Fig. 1b).

Grain size plays a more significant role in birefringent materials that have anisotropic refractive indices. In this case, as seen in Figure 1c, light is refracted at each grain boundary since each grain in a random polycrystalline ceramic represents a discontinuity in refractive index. A strategy to improve the transparency of a birefringent ceramic is to ensure very fine grain sizes. Figure 1d depicts an anisotropic material with grain sizes in the nanocrystalline range. In this case light is not scattered at grain boundaries.

3. Role of oxygen vacancies on optical properties

As discussed above, porosity and grain size can scatter light, reducing the inline transmission of ceramics. By contrast, point defects can absorb light, lowering the overall light transmission. Impurities almost always exist in engineered ceramics and some of these can serve as light absorption centers. Particularly common point defects in CAPAD-produced ceramics are oxygen vacancies. The majority of CAPAD experiments are done using graphite dies. A drawback of graphite dies in the optical ceramic case is that the as-processed ceramics are often dark and consequently have decreased transparency. It is often thought that darkening is caused by carbon contamination from the die. Carbon diffusion is likely to occur very near the interface between the ceramic and the die. However, the short CAPAD processing times preclude carbon from diffusing deep into the ceramic. Thus the near-interface layer can easily be polished off, resulting in a clean transparent ceramic.

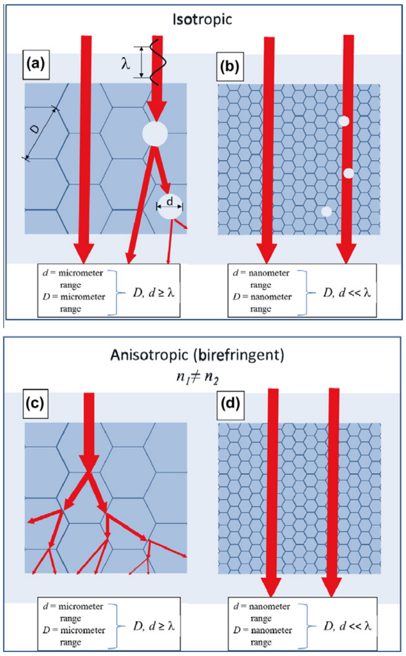

Figure 1. Schematic representations of the interaction of light with polycrystalline ceramics.

Instead of carbon contamination, it has been shown that in ceramics that have fast oxygen diffusion, darkening is caused by oxygen reduction, i.e. by the samples having an oxygen-deficient stoichiometry. Anselmi-Tamburini et al. conducted an experiment that clearly shows this to be the case [2]. A zirconia sample was processed in a graphite die between beds of coarse alumina powder to ensure that the sample is not in contact with carbon. Figure 2 shows a picture adapted from Ref. [2]. The edges of the sample are darker than the middle, suggesting that since carbon could not have diffused through the porous alumina powder, oxygen reduction must be responsible for darkening.

The reduction is caused by the very low partial pressure of oxygen that is developed in the high-temperature graphite during processing. Light absorption by oxygen vacancies with trapped electrons leading to darkening has been well documented in the yttria-stabilized zirconia (YSZ) case [3–5]. Figure 3 shows pictures of YSZ from the work of Casolco et al. [4]. These samples are densified at three different processing times—the longer the hold time, the more oxygen deficient and the darker the sample. Fortunately, it has been shown that the darkening caused by oxygen deficiency in many CAPAD ceramics can be easily reduced by annealing the samples in air.

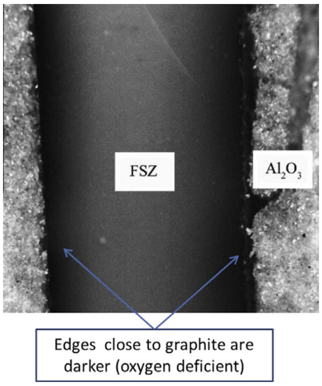

Figure 2. Optical micrograph showing darkening in zirconia densified between a bed of coarse alumina powder. The edges near the graphite are darker due to oxygen reduction caused by low oxygen partial pressure (modified with permission from Ref. [2]).