Quantification of SiO$_2$ sintering additive in YAG transparent ceramics by laser-induced breakdown spectroscopy (LIBS)

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Abstract: Transparent ceramics are important optical materials with applications in street lighting, high-strength windows, electro- and magneto-optical isolators, high-power laser gain media and radiation detectors. Their fabrication most often relies on powder densification techniques carried out at high temperatures, sometimes promoted by sintering additives. Here, we describe the application of laser-induced breakdown spectroscopy (LIBS) for following the concentration levels of silica used as a sintering agent in the fabrication of yttrium aluminum garnet (YAG) transparent ceramics. The sensitivity limit of our protocol reaches a few tens of ppm of silica in YAG ceramic samples, showing that LIBS can be implemented reliably for the rapid assessment of sintering additives in advanced ceramic processing.

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References and links


1. Introduction

Various ceramic applications require the sintering of powders to full density so as to enhance their structural, electronic or optical characteristics [1]. In many instances, this is accomplished by adding inorganic additives, at a percent level or less to ceramic powders, to help control the mobility of pores relative to the grain-boundaries during firing [2]. Monitoring the concentration of these additives throughout the ceramic fabrication process is integral to understanding their role on the evolution of the microstructure and to the optimization of the densification process. This state of affairs is well exemplified by the fabrication of pore-free, optically transparent, yttrium aluminum garnet (YAG, \( \text{Y}_3\text{Al}_5\text{O}_{12} \)) laser ceramics [3]. These ceramics are either fabricated by the densification of YAG raw powders [4] or by reactive sintering of aluminum oxide and yttrium oxide powders [5] using silicon oxide as sintering aid, introduced as a fine soot or from the hydrolysis of tetraethyl orthosilicate (TEOS, \( \text{C}_2\text{H}_5\text{O}_4\text{Si} \)). Compared to silica soot, the latter provides a better incorporation of \( \text{SiO}_2 \) by coating the starting powders uniformly. However, the exact amount of silica introduced through this method may not be known precisely due to the limited surface hydration of the powders (reagent-limited reaction), and possible evaporation loss of TEOS. Additionally, it was shown that, within the solubility limit in YAG, higher concentrations of \( \text{SiO}_2 \) decrease both the sintering time and the temperature [6]. However, in some cases a segregation of silicon-rich phases has been observed at grain boundaries after sintering [7] and a strong linear correlation has been evidenced between the amount of silica
and the broadband absorption loss in the visible and near-infrared [8]. Hence, recent fabrication efforts have aimed at reducing the amount of silica to limit the effect of such background absorption in this laser host, while allowing the fabrication of fully transparent parts.

This work investigates the use of Laser-Induced Breakdown Spectroscopy (LIBS) to quantify the amount of silica at various stages of the fabrication of YAG transparent ceramics. LIBS is an atomic emission spectroscopy technique that utilizes the emission of laser-induced plasmas for elemental identification and quantification. In contrast to Glow-Discharge Mass Spectroscopy (GDMS), LIBS is characterized by the ease of sample preparation, the ability to analyze samples in situ and in any physical state (powder, powder compact, sintered ceramic) with a spatial resolution as small as 5 µm [9–18]. LIBS is now a well-established technique for the quantitative analysis of trace, minor and major elements [15–17]. Quantitative analysis is commonly carried out by building a calibration curve with a set of certified reference materials (CRM). However, the challenge of such approach resides in the avoidance of matrix effects [19–21]. Although not all transparent ceramic samples have a matrix-matched reference material to quantify trace elements against, there are different strategies to simulate matrix effects and build a calibration curve [22–24]. This letter presents the quantification of trace and minor levels of silica in YAG green bodies and ceramics using the LIBS technique. This capability adds to current development aiming at providing detailed composition analysis, including stoichiometry, to improve the optical quality and fabrication consistency of YAG transparent ceramics [25].

2. Experimental

The green bodies and ceramics used in this study were prepared following a well-established protocol described in [26] and outlined in Fig. 1. High-purity aluminum oxide (Taiimei, 4N, 0.2 µm) and yttrium oxide (Nanocerox, 4N, 0.05 µm) powders were mixed in stoichiometric amounts. The sintering additive was introduced to the blend in the form of SiO₂ powder, (99.99%, Sigma-Aldrich, USA) or TEOS (99.999%, Sigma-Aldrich, USA) at a mass fraction of 0.5 wt% for silica and 0.5 and 20 wt% for TEOS, respectively. The powder mixtures were ball-milled, spray-dried and pelleted using dry uniaxial pressing followed by cold isostatic pressing to form compact green bodies. The pressed samples were calcined in air at 600°C for an hour, sintered in vacuum (10⁻⁶ torr) at 1735°C for 16 h, and subsequently annealed in air at 1100°C for 100 h. The amount of silica was measured at various stages during the process (identified by asterisks in Fig. 1) by sampling pellets after cold isostatic pressing, calcination and vacuum sintering.

A set of calibration samples was prepared using a stoichiometric mixture of aluminum oxide and yttrium oxide powders. Silica powder was added to obtain powder compacts with 0, 0.17, 0.64, 0.84 and 1.08 wt% SiO₂ respectively. The experimental error on the silica loading is 0.02% due to weighing uncertainties. These mixtures were homogenized in the presence of ethanol in an alumina mortar, dried and uniaxially pressed to form powder compacts. This protocol ensures that chemical matrix effects do not influence the quantification of silica [21].

The LIBS experiments were carried out on a J200 Tandem LA-LIBS system (Applied Spectra Inc.). The laser ablation was performed using a 8 ns, 266 nm Q-switched Nd:YAG laser operated at a repetition rate of 10 Hz. The laser pulse energy received by the sample was 14.7 mJ over a spot size of 100 µm, a size much larger than the individual particles and crystallites of the powder compacts and ceramics. The plasma emission was analyzed with a Czerny–Turner spectrometer (Isoplane, Princeton Instrument) with a 3600 grooves/mm grating centered at 288 nm, equipped with an ICCD detector (PIMAX4, Princeton Instrument). The gate delay and width were found optimal at 0.8 and 3 µs, respectively. Hundred spectra were accumulated on a single location to improve the signal-to-noise ratio, and this acquisition was repeated, for each sample, over 12 different locations on a 4x3 spot
grid over a 1.2x1 mm² area to average any possible sampling inhomogeneities during the ablation process (Fig. 2(a)).

The shot-to-shot fluctuations of the LIBS signal collected from 12 spots on a sample with SiO₂ loading of 0.838 wt% is shown in Fig. 2(b). The grey area in the figure represents the variation in the signal and the solid red curve is the average spectrum.

3. Results and discussion

Because of possible disparities in laser-to-sample coupling due to variations in sample density, it is expected that under identical ablation conditions, the temperature of the plasma vary and lead to quantification inconsistencies. This effect, however, can be minimized by using spectral lines of major matrix elements to normalize the analyte peak intensity. This normalization follows from Boltzmann’s equation applied to these emitters, and writes, at a plasma temperature $T$ [19]:

$$
\frac{I_{j \rightarrow E_\text{u}}}{I_{j \rightarrow E_\text{u}}} = \frac{N_j(T)Z_j(T) \cdot e^{-\frac{E_j-E_u}{kT}}}{N_j(T)Z_j(T)}
$$

(1)

where $N_j$ is the concentration of plasma species $k$, with partition function $Z_j$, emitting spectral lines of intensity $I_{j \rightarrow E_\text{u}}$ from upper levels of energy $E_j$. Hence, the influence of the plasma temperature on the intensity ratio can be minimized by choosing emitting levels whose difference in energy is small compared to $kT$. The silicon content in the YAG samples was then measured using the integrated intensity ratio of neutral silicon (288.158 nm) and neutral yttrium (288.654 nm) lines. The close proximity of the upper energy levels for these two transitions ($\Delta E \sim 0.6$ eV), relative to assessed plasma temperatures (on the order of $kT \sim 1-2$ eV), helps minimize matrix effects caused by difference in laser-sample interaction. Spectral emission lines were identified using the National Institute of Standard and Technology (NIST) database [27]. It should be noted that neither self-absorption nor interference effects with other elements present in the plasma were observed for the two lines used in this analysis.

The calibration curve was obtained using purposely made samples and is shown in Fig. 3. In this figure, the normalized peak area of the Si line, $A_S$, is plotted and fitted against the concentration of SiO₂, $W_{SiO_2}$ present in the YAG samples using a linear regression, $A_S = m \cdot W_{SiO_2}$.
The relative standard deviation (RSD) of the emission intensities ranges from 4 to 9%. The limit of detection (LOD) for SiO$_2$ was found to be 61 ppm in weight following the definition \( \text{LOD} = 3 \cdot \sigma_{\text{blank}} / m \), where \( \sigma_{\text{blank}} \) is the standard deviation of LIBS signal from blank sample. Using this calibration curve, the amount of SiO$_2$ was monitored during the entire fabrication process of transparent YAG ceramics made by reactive sintering (Table 1). In a sample batch in which an initial amount of 0.5 wt% of TEOS was added to the powder mixture of raw oxides (i.e. an equivalent of 0.166 wt% of SiO$_2$), we find that the mass of SiO$_2$ is actually 24% lower than expected. This drop, well outside the error bars of the quantification model, can be attributed to the reagent-limited hydrolysis of TEOS during ball-milling leading to the evaporation of any TEOS excess during spray-drying. A further decrease of 6% occurs during the calcination of the sample at 600°C in air, followed by a major loss of 60% in the sintered sample, totaling a cumulative loss of SiO$_2$ up to 71%. This last departure of silica results from the formation of volatile silicon suboxides, SiO$_x$ (x<2), during vacuum sintering at temperature above 1600°C [8].

Fig. 2. (a) Picture of an optical ceramic sample analyzed in the study. The inset shows the ablation craters left after the LIBS analysis. (b) Representative emission spectrum of a YAG ceramic analyzed by LIBS. In this example, the concentration of silica is 0.838 wt.%. The grey area in the figure represents the 1-sigma standard deviation of the signal and the solid red curve is the average spectrum.

Fig. 3. Calibration curve for the determination of SiO$_2$ concentration in YAG ceramics. The standard deviation of the blank sample is ± 0.0017.
Table 1. Evolution of the concentration of SiO\textsubscript{2} during the fabrication of a transparent YAG ceramic sample made by reactive sintering of Y\textsubscript{2}O\textsubscript{3} and Al\textsubscript{2}O\textsubscript{3} powders and doped with 0.5wt\% TEOS.

<table>
<thead>
<tr>
<th>Ceramic sample state</th>
<th>SiO\textsubscript{2} (wt.%)</th>
<th>Incremental loss of SiO\textsubscript{2} (%)</th>
<th>Cumulative loss of SiO\textsubscript{2} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder mixture before drying</td>
<td>0.145</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Green body</td>
<td>0.111</td>
<td>24</td>
<td>24</td>
</tr>
<tr>
<td>Green body calcined at 600°C</td>
<td>0.104</td>
<td>6</td>
<td>28</td>
</tr>
<tr>
<td>Sintered ceramic at 1735 °C</td>
<td>0.041</td>
<td>60</td>
<td>71</td>
</tr>
</tbody>
</table>

For comparison purposes only, a green body loaded with a large amount of TEOS (20 wt.\%, an amount too large to produce transparent YAG ceramics) lost 98\% of its silica content after firing, whereas a powder compact made with silica soot lost 88\% after sintering (Fig. 4). These results illustrate that the exact amount of silica loss varies greatly and depend on the fabrication protocol [10]. The figures above are only representative of the fact that large amounts of silica can be outgassed from the ceramic during extended firing, and that, in such open systems, the amount of silica participating to the densification of YAG is a hard figure to control.

![Fig. 4. Evolution of the SiO\textsubscript{2} content in green bodies and sintered ceramics of YAG for different initial amounts of silica precursors.](image)

4. Conclusions

This work details the protocol for the analysis of silica sintering additive in YAG ceramics by the LIBS technique. It shows that LIBS can be used to monitor the evolution of silica throughout the ceramic fabrication process from powdery samples, powder compacts, and fully-sintered transparent ceramics. The quantification of silica was accomplished using a calibration curve and the present limit of detection of our system amounts to 61ppm. Our results show that the large amounts of silica evaporated during the vacuum sintering of YAG ceramics at high temperatures can be monitored easily by LIBS and that this loss may help reduce the impact of this additive on the optical performance of YAG laser ceramics. We believe that this technique and similar protocols will help better understand the role of sintering additives and control their effects in the processing of advanced ceramics.