Importance of Compound Standards for EPMA of Garnet Laser Materials

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INTRODUCTION

Garnets such as Y3Al5O12 (YAG) and Gd3Ga5O12 (GGG) are often used as laser host materials. These host materials can be doped for laser activity with several mol% of Yb2O3, which is the substitution of Y by Yb. Electron probe microanalysis (EPMA) is often used to measure dopant concentration profiles in these laser materials to determine the segregation at crystal growth. But for quantitative EPMA it is essential to have the correct types of reference materials or standards. Undoped YAG and GGG single crystal compound standards and Yb2O3 (used for the present work) or Yb-glass standards are commercially available.

Using a commercial Yb2O3 standard combined with a commercial host material standard, or using only commercial phosphate standards, can lead to a difference in cation ratio compared to the ideal 3/5 cation ratio of garnets. This was found for Yb:YAG and Yb:GGG single crystal fibres (Figure 1) grown by the micro-pulling-down method and measured in a JEOL Hyperprobe 8500F. But a difference in cation ratio to the ideal garnet cation ratio is discussed as a local source of strain in these materials.[3] Therefore reliable concentration measurements with a high spatial resolution are needed. The cation ratio was determined to be close to the expected ideal 3/5 garnet ratio by inductively coupled plasma atomic emission spectroscopy (ICP-AES) in an average volume of the fibers. This average volume measurement can be compared with local electron probe microanalysis measurements, because the measured cation ratios do not change for all measurement points.

MATERIALS AND METHODS

Materials

To prepare the standard and the fibre crystal Yb:O3 (Auer-Remy GmbH), Al2O3 and Y2O3 (Alfa-Aesar) powdered materials of at least 4N purity were used.

Preparation of Standards

Standards for this system can be prepared by solid-state sintering. Here we describe how we prepared a standard for Yb:YAG.

5 g total weight of powdered Yb2O3, Al2O3, and Y2O3 of 4N purity were mixed and ground in ethanol using a zirconium oxide ball mill. The powders were then dried, pressed into pellets isostatically at 200 MPa and sintered at 1400°C for 24 hours in platinum crucibles. This was repeated twice with the reground pellet. After this process the pellet was phase pure but still of low density. Therefore a final step the pellet was sintered again at 1750°C for 10 hours on a low density Al2O3 ceramic sheet. The resulting pellet was dense, milky white and slightly translucent.

A rim with a thickness of 1 mm was cut from the pellet to avoid impurities which might have come from contact with the Al2O3 ceramic sheet during the sintering process. From the resulting pellet a sample 2×2×2 mm2 in size was cut out from the middle of the pellet for use as our standard. The residual parts of the pellet were used for X-ray powder diffraction (XRD) and ICP-AES measurements. The X-ray powder diffraction showed phase purity.

Specimen Preparation for EPMA

The standard piece and cut single crystal fibre pieces were embedded in methyl methacrylate (Heraeus-Kulzer Technovit 5071) into holes of nearly the size of the specimen in a one inch glass disc to keep contamination in the microprobe due to outgassing of the resin as low as possible. The glass disc was then ground on SC paper of 200, 400, 800 and 1200 grading. Then the disc was polished on felts with 12, 9, 6, 3 and 1 µm diamond suspensions. A thin film of carbon was then evaporated on the surface to provide conductance.

Electron Microprobe Microanalysis

EPMA was performed on a JEOL hyperprobe 8500F thermal field-emission electron microprobe with four WDS spectrometers. Measurements were made on the ceramic standard sample with different accelerating voltages and different standards (Table 2). Counts were made on the peak of the element and to the left and right of the peak for the background. Detailed conditions for the three elements can be found in Table 1.

Inductively Coupled Plasma Atomic Emission Spectroscopy

For the ICP-AES measurements 300 mg of the samples of the single crystal fibre or the Yb:YAG ceramic standard were dissolved in 50 ml of a mixture of H3PO4 and HNO3 acids.

Figure 1: Photograph of a Yb:YAG fibre grown by the micro-pulling-down method.

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BIOGRAPHY

Dirk Maier received a diploma in physics from the University of Tübingen in 2002 and a PhD on segregation effects in crystal growth of single crystalline fibres from the Leibniz Institute for Crystal Growth. His research interests are in the growth and characteristics of oxide and fluoride single crystals and their characterization by electron probe microanalysis and X-ray powder diffraction.
We used a Thermo Fisher Scientific IRIS Intrepid HR Duo ICP-AES system equipped with an argon-rinsed Echelle polychromator (Echelle grating of 52 mm⁻¹) and a CID camera for registration of emission spectra. The wavelength range was 165–1000 nm and the spectral dispersion at 200 nm 0.0035 nm pixels⁻¹. The photosensitive area of the CID camera was 14.3 × 14.3 mm² or 512 × 512 pixels, respectively. The plasma was observed axially. The ICP-AES measurements compared the intensity of spectral lines from the sample with that from simple solution calibration standards (Bernd Kretz, Duisburg, Germany). The precision was ±1% relative standard deviation for concentrations above background equivalent concentration.

**X-Ray Powder Diffraction**

For XRD measurements the cut parts of the sintered sample were milled in a ZrO₂ ball mill and fixed with a film of silicon grease onto a steel sample holder. The measurements were performed in a Seiffert URD 6 diffractometer operated at 40 kV and 40 mA using Cu K-alpha radiation. The silicon grease is responsible for the irregular bump in the background between 10° and 25°. The plasma was observed axially. The ICP-AES measurements compared the intensity of spectral lines from the sample with that from simple solution calibration standards (Bernd Kretz, Duisburg, Germany). The precision was ±1% relative standard deviation for concentrations above background equivalent concentration.

**Results and Discussion**

It was observed from the ZAF correction factors used by the microprobe software that aluminium and yttrium have to be corrected more than 20%. The mass attenuation coefficients found in published tables [4] of aluminium K-alpha in ytterbium (1464 cm² g⁻¹) are close to the mass attenuation coefficients of aluminium K-alpha in yttrium (1501 cm² g⁻¹), but the mass attenuation coefficient for yttrium L-alpha in yttrium (3514 cm² g⁻¹) is much higher than for yttrium L-alpha in ytterbium (803 cm² g⁻¹), so in the case of the substitution of only several mol% yttrium by ytterbium, the calculated absorption correction factors for aluminium are only slightly changed, whereas for yttrium higher corrections are needed. And because of the overestimation of Al and the underestimation of Y it can be concluded that in the Yb:YAG matrix the mass attenuation coefficient for Al K-alpha in Yb is higher and that for Y L-alpha in Yb is lower than the mass attenuation coefficients found in published tables or used by the correction tables.

**Table 1:** Detailed experimental electron probe microanalysis conditions used for the measurement of the three elements Al, Y and Yb.

<table>
<thead>
<tr>
<th>Element</th>
<th>Detector crystal</th>
<th>Counting time Peak / Background (sec)</th>
<th>Beam current (nA)</th>
<th>kV</th>
<th>Counter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al K-alpha</td>
<td>TAP</td>
<td>30 / 15</td>
<td>40</td>
<td>12</td>
<td>Gas flow proportional counter</td>
</tr>
<tr>
<td>Y L-alpha</td>
<td>TAP</td>
<td>30 / 15</td>
<td>40</td>
<td>12</td>
<td>Xe-filled proportional counter</td>
</tr>
<tr>
<td>Yb L-alpha</td>
<td>LIF</td>
<td>60 / 30</td>
<td>40</td>
<td>12</td>
<td>Gas flow proportional counter</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Measured Composition in Cation Numbers with O = 12</th>
<th>Accelerating Voltage kV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃ / Y₂O₃ / Yb₂O₃</td>
<td>YbPO₄ and YAG compound</td>
</tr>
<tr>
<td>5.215 / 2.325 / 0.460</td>
<td>12</td>
</tr>
<tr>
<td>5.215 / 2.325 / 0.460</td>
<td>YbPO₄ and YAG compound</td>
</tr>
<tr>
<td>5.035 / 2.530 / 0.435</td>
<td>Yb:YAG compound</td>
</tr>
</tbody>
</table>

normally, decreasing the accelerating voltage reduces the absorption correction, but because the wrong mass attenuation coefficients were used in the calculation of the absorption correction factors a lower accelerating voltage does not lead to better results in this case. This is shown for two measurements at 12 kV and 20 kV (Table 2). Therefore a Yb:YAG compound standard with a composition close to the measured sample has to be chosen to minimize the effect of the wrong absorption correction (Table 2). But such standards are not available commercially. Therefore we prepared a compound standard by solid-state sintering. In this standard grains larger than 5 µm and with low porosity were found by imaging with backscattered electrons (Figure 3). But one can also see white particles which were identified as ZrO₂. These particles were introduced as a result of abrasion from the ball mill and did not alter the composition needed for standardization. EPMA measurements of several grains showed good homogeneity; indeed some grains looked brighter than others in the BSE image.

From the ICP-AES measurements the composition of the new standards was found to be 41.08 ± 0.38 wt% Al₂O₃, 45.35 ± 0.37 wt% Y₂O₃ and 13.58 ± 0.06 wt% Yb₂O₃, which is Y₂.₅₂Yb₀.₄₃Al₀.₄₂O₃ as a chemical formula. The composition obtained by ICP-AES was then used for EPMA standardization. When the crystal fibres above were then measured using this ceramic compound standard the resulting cation ratios were found to be equal to the ratios measured by ICP-AES. This can be seen in Table 2 when the measurements were done on the Yb:YAG standard sample.

**Conclusions**

Using a combination of commercially available standards such as YbPO₄ and undoped YAG, or just phosphate standards, for quantitative EPMA measurements of Yb:YAG leads to the wrong quantification, even in the case when using a lower accelerating voltage to reduce absorption effects. It was shown that a Yb:YAG ceramic standard can be prepared by solid-state sintering and referenced by induction coupled plasma atomic emission spectroscopy. Using such a ceramic compound standard leads to correct quantification.

**References**

5. The International Center for Diffraction Data ICDD, PDF card no. 00-033-0340.