Yb₃⁺ distribution and lattice parameters of Yb:YAG crystals

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Abstract

YbₓY₃₋ₓAl₅O₁₂ crystals with different Yb³⁺ concentration have been grown by the Czochralski method. The distribution coefficient of Yb³⁺ is 1.08 ± 0.01, and it has little relation with Yb³⁺ concentration. The lattice parameter of YbAG is 1.193799 ± 0.000054 nm. We have found an equation connecting the lattice parameter and Yb³⁺ concentration: a(γ) = 1.200976 – 0.007072x nm.

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1. Introduction

Recent development of InGaAs diode laser has stimulated interest in Yb³⁺ doped solid state materials to be used as gain for high efficiency, high power diode-pumped solid state lasers [1]. The trivalent ytterbium ion’s simple [Xe]⁴⁴¹³ electronic structure allows for no excited state absorption, upconversion or concentration quenching. The small stokes shift (about 650 cm⁻¹) between absorption and emission reduces the thermal loading of the material during laser operation.

Among the numerous Yb-doped crystals, Yb:YAG has many other attractive characteristics such as high thermal conductivity, excellent physical and chemical properties of the host material. Moreover, because of broad absorption band suited for diode-pumping, relatively larger laser transition cross section, the lowest heat generation of any diode-pumped solid-state laser medium, and high quality and highly doped crystals which can be easily grown, Yb:YAG crystal has become an important component in diode pumped high power laser systems [2]. In less than a decade, diode-pumped Yb:YAG lasers have increased in average output power from 23 mW [1] to 2.65 kW [3], catching up with that of Nd:YAG [4].

In this paper, the distribution coefficients of a series of Yb³⁺ doped YAG crystals grown by...
Czochralski method were studied, and the lattice parameters of Yb:YAG crystals were also analyzed.

2. Experimental procedure

2.1. Crystal growth

The YAG, Yb:YAG and YbAG crystals used in this study were grown using the Czochralski technique [5]. The 99.999% grade raw materials were appropriately pre-dried and weighted according to a definite molar ratio, and uniform mixing was carried out in a ball mill coated with polyethylene. The mixture was pressed into blocks with a diameter close to the inner diameter of the crucible at high pressure and then sintered in an aluminum crucible at 1350°C for 24 h. The charge was then loaded into the Ir crucibles for crystal growth.

The optimal growth conditions were found to be as follows: rotation rate 10–20 rpm, pull rate 1 mm/h under the nitrogen or argon atmosphere. The initial growth boundary in solid-melt was convex towards the melt so that the dislocations and impurity were reduced or eliminated. After that, the growth boundary became flat. In order to prevent the crystal from cracking, the crystal was cooled to room temperature slowly after growth.

2.2. Sample preparation

The sample was cut from the crystals adjacent the seed crystal positions, and then was grinded to powder in an agate mortar for measurement. The powder was analyzed with Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) for Yb³⁺ concentration. The crystal structures are measured by JUINER HAJJ Camera. The data have been collected and analyzed by computer.

3. Results and discussion

3.1. Distribution of Yb³⁺

When the dopant come from the melt phase into the crystal phase, its concentration has a change as the distribution coefficient \( k_m \) is not equal to 1. If \( k_m > 1 \), the ion concentration in the crystal is larger than that in the melt, and it is becoming lower from the top to the bottom of the crystal in the processing of crystal growth, so a concentration gradient appears. Such gradient is detrimental to the laser performance of Yb:YAG.

The distribution coefficient of Yb³⁺ in Yb:YAG crystals can be calculated by the following formula:

\[
k_m = \frac{c_{\text{top}}}{c_0},
\]

where \( c_{\text{top}} \) is the Yb³⁺ concentration at the growth starting position in the crystals, and \( c_0 \) is the initial Yb³⁺ concentration in the melt.

The Yb³⁺ concentrations of various samples analyzed by ICP-AES are listed in Table 1, and \( k_m \) is calculated using Eq. (1). We can conclude that the distribution coefficient of Yb³⁺ in Yb:YAG crystals grown by Czochralski technique is 1.08 ± 0.01. Yb³⁺ concentration has little influence on the distribution coefficient of Yb³⁺ in Yb:YAG crystals. The yttrium and ytterbium garnets are isostructural with only a 1.5% difference in unit-cell size [6]. As a result Yb can easily substitute the Y site in the dodecahedron, and the distribution coefficient of Yb³⁺ is close to 1.

3.2. Structure

The compositions of Yb:YAG crystals are made of three oxides (Y₂O₃, Al₂O₃ and Yb₂O₃). In the Yb:YAG crystals the Yb³⁺ ion is in the place of the Y³⁺ site in a dodecahedron. From the results of the crystal structure analysis the lattice

<table>
<thead>
<tr>
<th>Samples</th>
<th>( c_0 ) (at%)</th>
<th>Atom content (wt%)</th>
<th>( c_{\text{top}} ) (at%)</th>
<th>( k_m )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>41.94</td>
<td>4.70</td>
<td>5.44</td>
<td>1.09</td>
</tr>
<tr>
<td>Yb</td>
<td>39.71</td>
<td>9.82</td>
<td>10.72</td>
<td>1.07</td>
</tr>
<tr>
<td>C</td>
<td>36.14</td>
<td>13.68</td>
<td>16.28</td>
<td>1.09</td>
</tr>
<tr>
<td>D</td>
<td>32.54</td>
<td>17.64</td>
<td>21.78</td>
<td>1.09</td>
</tr>
<tr>
<td>E</td>
<td>29.78</td>
<td>21.55</td>
<td>27.10</td>
<td>1.08</td>
</tr>
<tr>
<td>F</td>
<td>16.65</td>
<td>37.48</td>
<td>53.63</td>
<td>1.07</td>
</tr>
</tbody>
</table>
parameters are given in Table 2. It shows that the structures of various Yb\(^{3+}\) doped YAG crystals are similar to that of pure YAG and have a cubic symmetry with space group Ia\(_3d\). The lattice parameters of YAG and YbAG are \(1.201159 \pm 0.000034\) and \(1.193799 \pm 0.000054\) nm, respectively, and there is only a 1.8% difference in unit-cell size. The data agrees with that in Ref. [6]. Fig. 1 shows the Yb\(^{3+}\) concentration dependence of lattice parameter. It can be seen that lattice parameter is a linear function of Yb\(^{3+}\) concentration, and with the Yb\(^{3+}\) concentration increases, the lattice parameter drops. In rare earth yttrium aluminum garnets ionic radius \(r \) dependence on lattice parameter \(a \) is as follows [7]:

\[
z = K_C(r_C) + K_A(r_A) + K_D(r_D),
\]

(2)

Table 2

<table>
<thead>
<tr>
<th>Yb(^{3+}) concentration (at%)</th>
<th>(a) (nm)</th>
<th>(\beta)</th>
<th>(V) (nm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.201159 \pm 0.000034</td>
<td>90.0</td>
<td>1.73301</td>
</tr>
<tr>
<td>5.44</td>
<td>1.200424 \pm 0.000063</td>
<td>90.0</td>
<td>1.72983</td>
</tr>
<tr>
<td>10.72</td>
<td>1.200058 \pm 0.000043</td>
<td>90.0</td>
<td>1.72825</td>
</tr>
<tr>
<td>16.28</td>
<td>1.199765 \pm 0.000058</td>
<td>90.0</td>
<td>1.72699</td>
</tr>
<tr>
<td>21.78</td>
<td>1.199439 \pm 0.000042</td>
<td>90.0</td>
<td>1.72558</td>
</tr>
<tr>
<td>27.10</td>
<td>1.199214 \pm 0.000038</td>
<td>90.0</td>
<td>1.72461</td>
</tr>
<tr>
<td>53.63</td>
<td>1.197364 \pm 0.000065</td>
<td>90.0</td>
<td>1.71664</td>
</tr>
<tr>
<td>100</td>
<td>1.193799 \pm 0.000054</td>
<td>90.0</td>
<td>1.70135</td>
</tr>
</tbody>
</table>

Fig. 1. Lattice parameter as a function of Yb\(^{3+}\) concentration.

where \(r_C, r_A\) and \(r_D\) are the effective radius of central caution in tetrahedral, octahedral and dodecahedra, respectively. \(K_C, K_A\) and \(K_D\) are constants. For our experimental results the lattice parameter \(z\) is in good agreement with the rule of lattice selection and ionic radius. The smaller radius of Yb\(^{3+}\) ion (0.0985 nm) is in the place of larger radius Y\(^{3+}\) (0.1019 nm). Fig. 1 shows that the structural distortion is small with various Yb\(^{3+}\) concentration in Yb:YAG and we get a linear equation to show the relation between lattice parameter and Yb\(^{3+}\) concentration. The equation is as follows:

\[
z(x) = 1.200976 - 0.007072x\ \text{nm}.
\]

From the equation, we could estimate the densities of crystals with different Yb\(^{3+}\) concentration by the cell volume, molecular weight of Yb:YAG and the density of YAG.

4. Conclusion

Different Yb\(^{3+}\)-doped Yb:YAG crystals have been grown by the Czochralski method. The distribution coefficients of Yb:YAG crystals with different concentrations of Yb\(^{3+}\) ions were measured. Our results show that the doping concentration of Yb\(^{3+}\) has little influence of the distribution coefficients. The lattice parameters of various concentrations of Yb:YAG crystals have been analyzed. The lattice parameter of YbAG is \(1.193799 \pm 0.000054\) nm. We have found an equation connecting the lattice parameter and Yb\(^{3+}\) concentration: \(z(x) = 1.200976 - 0.007072x\ \text{nm}.

Acknowledgements

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References