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Spectral properties of hydrothermally-grown Nd:LuAG, Yb:LuAG, and Yb:Lu_2O_3 laser materials

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ABSTRACT

We have investigated the hydrothermal growth of, and spectrally characterized, the lutetium based laser materials Nd:LuAG, Yb:LuAG, and Yb:Lu_2O_3. Absorption cross-section data are presented for Nd:LuAG at 83, 175, and 295 K. Absorption cross-section data was also obtained for Yb:LuAG at 83, 175, and 295 K; the 295 K data was used to generate emission cross-sections using the method of reciprocity. For Yb:Lu_2O_3, we present absorption cross-sections at 295 K as well as emission cross-sections derived using reciprocity.

1. Introduction

It is well known that YAG ($Y_3Al_5O_{12}$) is an excellent host for trivalent lanthanide laser ions. It was first investigated very early as a solid-state host and has since received an enormous amount of attention. It has excellent physical and optical properties. It can be grown well using the Czochralski method, can be easily doped with a wide variety of trivalent ions, has outstanding thermal and chemical stability and has good thermal conductivity [1]. Because of the extensive investigation of the material, most of the optical transitions for most of the common lasing ions are well established and identified. The material is especially useful as the host for diode pumped solid state lasers (DPSSLs), whereby the YAG is doped with the desired lasing ion and pumped with a suitable diode [2,3]. The development of reliable high-powered diodes at a number of wavelengths, and the ability to manufacture and process the YAG crystals makes the general concept of DPSSLs especially attractive as a laser technology.

Over the years as workers have begun to look for improved hosts for use in DPPSLs, among the various hosts under investigation is the lutetium analog to YAG, $Lu_3Al_5O_{12}$ or LuAG. Like YAG it can be grown as high quality single crystals, can be readily doped with trivalent lasing ions, and has excellent thermal and chemical stability. Careful study of its optical properties, however, indicates that it is not merely a trivial substitute for YAG. Rather, there are some subtle and important factors that may make it a better host for some high performance DPSSL applications. In particular it has a wider bandgap than YAG (175 nm vs. 195 nm), it has a significantly higher refractive index (1.83 vs. 1.81 at 1.0 μm), and it has a slightly smaller lattice than YAG (11.92 Å vs. 12.01 Å for YAG). The smaller lattice size suggests that the host may have somewhat larger Stark splitting for the dopant lasing ions. This may have significant and favorable ramifications for the Boltzmann populations of the lower lasing states in quasi-three level lasers such as Yb^{3+} lasing at 1029 nm, and the 946 nm lasing line for Nd^{3+}. It should also be noted that with the exception of the relatively large Nd^{3+} lasing ion, most of the other common lasing ions including Yb^{3+}, Er^{3+}, Tm^{3+} and Ho^{3+} are all relatively small and hence very similar in size to the host Lu^{3+} in LuAG. This allows for smooth substitution of the dopant ions over a wide concentration range with minimal lattice distortion or strain.

One subtle but important point regarding LuAG as a host is related to its thermal conductivity. The thermal conductivity of pure YAG is reasonably high for an oxide (ca. 11 W/m K) while that of pure LuAG is slightly lower (ca. 9 W/m K). Upon doping however the situation changes somewhat. Since the atomic mass is quite different for the host yttrium vs. the dopant (Yb, Er, etc.) in YAG, the thermal conductivity of the crystal sample decreases significantly upon doping. Even at low doping concentrations the lasing ion acts as a lattice defect with respect to phonon

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conduction and reduces the thermal conductivity significantly. In contrast common dopant ions like Yb and Er have nearly identical mass as that of Lu. Therefore the thermal conductivity of doped LuAG does not decrease as much as doped YAG and is often very similar to the undoped material [4]. Thus in many cases the thermal conductivity of the doped material is often better for LuAG versus YAG, which leads to improved laser performance [5].

Investigations throughout the years have demonstrated that doped LuAG can display excellent lasing characteristics. For example Tm:LuAG [6] and Nd:LuAG [7] have been investigated in DPSSLs. Of particular interest is Yb:LuAG whose lasing properties have been studied by several groups [8–12]. The ytterbium dopant is particularly suitable in LuAG since it is adjacent to the host Lu in the periodic table and hence has nearly identical size, mass, and chemical properties, making it ideal as a dopant/host combination. Pulsed lasing has also been obtained using Cr^{4+} for passive Q switching in Yb:LuAG [13]. One interesting observation for Yb^{3+} doped into LuAG versus YAG is that the room temperature emission cross section for Yb^{3+} at 1030 nm was reported to be approximately 30% greater in LuAG versus YAG. This factor combined with its enhanced thermal conductivity relative to doped YAG (see above), make Yb^{3+} doped LuAG a very attractive potential host for high power and microlaser applications [5,8].

Other lutetium based oxide host crystals also show excellent potential as well. In particular Lu_2O_3 displays outstanding properties as a host for Yb^{3+} and similar dopants. It has excellent chemical stability, optical properties and thermal conductivity. The only drawback to its full-scale implementation is the difficulty in preparing high quality single crystals. Lu_2O_3 is exceptionally refractory with a melting point greater than 2450 °C. This leads to difficulties in growth of single crystals using classical melt based crystal growth methods, leading to substantial thermal strain and impurities from the growth crucibles. Despite the difficulties in preparing single crystals Petermann et al. were successful in growing single crystals of Lu_2O_3 doped with various concentrations of Yb^{3+} in particular, and obtained very promising laser data, confirming its inherent potential [14–17].

Recently, we used the hydrothermal method [18] to grow high quality single crystals of YAG [19], LuAG [20] and Lu_2O_3 [21]. Further we found that the crystals can be doped with a wide variety of relevant dopants, and that multiple epitaxial layers can be grown on the same substrate to create multifunctional single crystals to address a number of lasing problems [22,23]. Given the potential of LuAG and Lu_2O_3 as possible efficient high power laser hosts, especially in the 1-μm range, and our success in growing high quality single crystals using the hydrothermal method, we think it is important to obtain detailed spectroscopic analyses of doped LuAG and Lu_2O_3 crystals. Recently detailed analysis of Yb:LuAG appeared that included determination of absorption and emission cross sections of Yb:LuAG at variable temperatures between 20 and 200 °C. However it included no data at low temperatures and was also hampered by lack of accurate data of dopant concentration [24]. Detailed knowledge of all factors affecting cross sections and band energies can lead to the design of extremely efficient and high performing lasers [25–27].

In this paper we report the detailed analysis of the absorption spectra of Nd:LuAG at room and low temperatures, Yb^{3+} doped LuAG absorption and emission cross-sections at room and low temperatures, and absorption and emission cross-sections of Yb:Lu_2O_3 single crystals at room temperature. We calculate the energy levels due to ligand field splitting (Stark levels) within each spin orbit value and determine the resultant Boltzmann population to help determine the inversion values for lasing at various temperatures. Note that we focus here specifically on hydrothermally-grown single crystal data in contrast to the relatively large amount of work performed on doped transparent ceramics of the lutetium based oxide hosts [28,29]. This provides an important series of benchmark measurements for comparison of different materials prepared by different crystal growth techniques or processing methods.

2. Crystal growth

2.1. Hydrothermal growth of Nd:LuAG single Crystals

Hydrothermal crystals of Nd:LuAG were grown epitaxially on a YAG surrogate seed. The growth feedstock consisted of 1 g of crushed sapphire crystals (GT Crystal Systems, Salem MA) and 2.34 g of Nd:Lu_2O_3 (HEFA Rare Earth, 99.997%) feedstock. The lanthanide feedstock was pre-doped with 4% Nd^{3+} using a co-precipitation process described elsewhere [20] and this Nd concentration in the feedstock was sufficient to provide the 2.6% Nd concentration in the final crystal. A 5 mL solution of aqueous 2 M K_2CO_3 corresponding to a 60–70% fill of the reaction vessel was added to a welded 7.5 mm × 150 mm silver tube. YAG seeds with [1 0 0] orientation and dimensions of 10 mm × 5 mm × 2 mm were hole-drilled and tied securely using thin silver wire (Alfa Aesar, 0.1 mm dia., 99.997%) to the upper part of a ladder fashioned from thicker silver wire (Alfa Aesar, 1 mm dia., 99.99%) that serves to physically stabilize the seed while holding it in the correct temperature zone. The ladder was placed in the silver tube and after welding these sealed silver tubes closed, they were placed in Inconel autoclaves. The autoclaves contained enough water to provide the necessary counter pressure to prevent the tubes from bursting when heated. A temperature gradient of 610 °C to 640 °C, top to bottom, was established using two individually controlled ceramic band heaters with thermocouples affixed to the autoclave externally. The autoclave with band-heater setup was packed in vermiculite for insulation and the reaction was allowed to proceed undisturbed for 2–3 weeks. Autoclaves were then either slow-cooled naturally by discontinued heat over a 24-hour period or quick quenched by an air stream. Single crystals in the form of 1–2 mm thick epitaxial layers of the target compound with face sizes of 2 mm × 4 mm were then cut away from the surrogate YAG seeds by using a diamond wire-saw. These crystals were then prepared for optical characterization by polishing their faces with progressive lapidary discs starting with 1200 grit and ending with 100,000 mesh diamond spray.

2.2. Hydrothermal growth of Yb:LuAG single Crystals

Single crystals of Yb:LuAG were grown and prepared by a directly analogous method as the Nd:LuAG, except a premade 4% Yb:Lu_2O_3 powder was used as the lanthanide feedstock component. Here, the dopant concentration in the as-grown crystal was determined to be 3.6%. As one would expect there is less dopant ion partitioning in Yb:LuAG growth compared to Nd:LuAG, though the 2.6% Nd^{3+} doping achieved above is remarkably high for that system.

2.3. Hydrothermal growth of Yb:Lu_2O_3 single Crystals

Yb:Lu_2O_3 crystals used in the present study were grown on seed crystals from previous hydrothermal growth experiments [21]. Specifically, these crystals were grown from a feedstock consisting of a mixture of Lu_2O_3 (HEFA Rare Earth, 99.997%) and Yb_2O_3 (Alfa Aesar, 99.9%), with a nominal Yb_2O_3 concentration of 4%. Here, 20 M KOH was used as a mineralizer, and the crystal growth again occurred as above in a sealed silver ampoule within the Inconel autoclave. A temperature gradient of 630–660 °C was maintained from top (growth zone) to bottom (dissolution zone)