Crystal Growth and Phase Stability of Ln:Lu₂O₃ (Ln = Ce, Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, Tm, Yb) in a Higher-Temperature Hydrothermal Regime

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Abstract

A higher-temperature hydrothermal approach (650-700 °C) has been employed in the crystal growth of Lu₂O₃ and its lanthanide-doped analogs. Carefully controlled thermal gradients of 30 degrees or less were also used to minimize the number of nucleation sites. The resulting crystals exhibit improvements in size and optical clarity over those grown at 600-650 °C. These outcomes are likely also attributed to a greater stability of Lu₂O₃ relative to LuO(OH) at the higher temperature conditions. The doping of Lu₂O₃ single crystals has been extended to encompass all spectroscopically active trivalent rare earth ions. Absorption spectra have been obtained of a wide range of lanthanide-doped Lu₂O₃ single crystals from 80-298 K and the spectra of Nd:Lu₂O₃ are reported as a representative example herein.

Keywords: A2. Hydrothermal crystal growth; A2. Single crystal growth; B1. Oxides; B1. Rare earth compounds; B3. Solid state lasers

1. Introduction

The development of single crystals for optical applications continues to be an important motivator for many crystal growth researchers. Recently, the rare earth sesquioxides, Sc₂O₃,

Y_2O_3 , and Lu_2O_3 , have emerged as extremely attractive optical materials, particularly for their potential as high power laser materials [1-3]. These materials all possess relatively high thermal conductivities, high thermal stability, suitably broad absorption bands, a wide transparency range, and a cubic crystal structure, all of which are very appealing characteristics for solid-state laser hosts [4,5]. In particular, Lu_2O_3 appears especially promising since Lu^{3+} offers a close size and mass match to many of the lanthanide dopant ions of interest, allowing the crystals to support high doping levels with minimal sacrifice of thermal conductivity [6-8]. Several recent studies have confirmed the potential of lanthanide doped Lu_2O_3 as a versatile optical material [9-14]. As such they make very attractive targets for single crystal growth studies.

The high melting point of Lu_2O_3 (2450 °C) presents significant technical challenges to the growth of single crystals by classical melt-based methods. Few traditional approaches have gained traction, and recent efforts in Lu_2O_3 crystal growth have converged on a few techniques. The micro-pulling-down method has been used to grow single crystals a few millimeters in diameter with lanthanide doping targeted for laser and scintillator applications [15-18]. Excellent progress toward larger crystals has been made using the heat exchanger method, which requires a delicate manipulation of the growth atmosphere to manage color centers and crucible activity [19,20]. These extreme crystal growth demands and promising materials characteristics of the sesquioxide systems prompted us to develop a unique hydrothermal approach to the growth of Sc_2O_3 and Lu_2O_3 [21,22]. Hydrothermal crystal growth of these materials can occur in a closed system at modest temperatures (550-650 °C), well below the melting point of the oxides using a supercritical aqueous hydroxide solution as a transport medium. Many refractory oxides are soluble under these conditions, and growth can occur either by spontaneous nucleation, or be deposited onto a seed crystal [23]. Previous spectroscopic studies of some of the initial

hydrothermally-grown Yb:Lu₂O₃ single crystals further supports their potential for optical applications [24,25].

A particularly attractive use is in cryogenic laser systems. In these cases most of the desirable properties of the high power lasers are enhanced by cooling the laser cavity to cryogenic (< 150 K) temperatures, with most lasers using liquid nitrogen at 77 K. The thermal conductivity of the laser crystal increases dramatically, most thermal distortion effects are eliminated and thermal population of the Stark levels in the ground electronic states are minimized. This latter point is particularly important because it can effectively convert room temperature three level laser systems to de facto four level systems at low temperature, which greatly reduces the necessary pump power and inversion threshold. This effect has already been observed in the case of Yb³⁺ [5, 26,27] but is not particularly well known for many of the other rare earth lasing ions. In an effort to generate a more comprehensive understanding of the behavior of rare earth ions in Lu₂O₃ single crystals we studied the doping of the trivalent lanthanides in hydrothermally grown lutetia crystals. Here we report an optimization of the hydrothermal growth process, and its extension to the entire palette of lanthanide dopants to grow single crystals of Ln:Lu₂O₃ (Ln = Ce, Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, Tm, Yb). Also, as an example of doping the larger early lanthanide ions in lutetia, we report preliminary absorption spectra of Nd:Lu₂O₃ at cryogenic temperatures and provide a direct comparison to the corresponding room temperature spectra.

2. Experimental

2.1. Crystal Growth of Ln:Lu₂O₃.

Single crystals of Lu_2O_3 and $\text{Ln}:\text{Lu}_2\text{O}_3$ ($\text{Ln} = \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}$) were grown hydrothermally from feedstock consisting of powders of the host and dopant oxides. All reagents were used as-purchased from commercial vendors: Lu_2O_3 (HEFA Rare Earth, 99.99%), Ce_2O_3 (CERAC, 99.9%), Pr_2O_3 (Alfa Aesar, 99.9%), Nd_2O_3 (Alfa Aesar, 99.9%), Sm_2O_3 (Alfa Aesar, 99.9%), Eu_2O_3 (HEFA Rare Earth, 99.9%), Tb_4O_7 (HEFA Rare Earth, 99.9%), Dy_2O_3 (Strem, 99.9%), Ho_2O_3 (HEFA Rare Earth, 99.9%), Er_2O_3 (Alfa Aesar, 99.99%), Tm_2O_3 (HEFA Rare Earth, 99.9%), Yb_2O_3 (HEFA Rare Earth, 99.99%).

Growth was performed in silver ampoules that were 3/8 in. o.d. and 6 in. in length, containing approximately 2 g of the oxide powder. For $\text{Ln}:\text{Lu}_2\text{O}_3$ growth, the host and dopant oxide powders were mixed in the desired molar ratio, targeting dopant concentrations of 1-10 at.% based on the lanthanides (for example, 5% $\text{Dy}:\text{Lu}_2\text{O}_3$ targets a stoichiometry of $\text{Dy}_{0.10}\text{Lu}_{1.90}\text{O}_3$). An aqueous mineralizer solution of 20 M KOH (4 mL) was added to the ampoule, and the ampoule was sealed by an arc weld. The ampoules were placed in a Tuttle cold-seal autoclave containing additional water as counter-pressure (1.5-2 kbar autogenously generated). The autoclave was heated to 650-700 °C, and a thermal gradient of 30 degrees was established along the length of the autoclave using external heaters to encourage crystal growth in the cooler regions of the ampoule. Phase stability studies were kept at these conditions for one week, while prolonged growth reactions were allowed to proceed for three weeks. After this period the autoclave was cooled to room temperature over a 12 hour period and the crystals harvested from the ampoules.

2.2. Characterization.

Phase stability in the $\text{Lu}_2\text{O}_3\text{-H}_2\text{O-KOH}$ system was evaluated by powder X-ray diffraction (PXRD). Data were collected on well-ground samples of composite reaction products obtained by hydrothermal reactions at a variety of temperatures. A Rigaku Ultima IV powder diffractometer equipped with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) was used to collect the diffraction data (5-65 degrees in 2Θ , scan speed of 1.0 deg/min). Phase identification was made by comparison to patterns indexed by the International Centre for Diffraction Data.

Semiquantitative elemental analysis of the $\text{Ln:Lu}_2\text{O}_3$ crystals grown as described above was performed using energy dispersive X-ray analysis (EDX) to determine the approximate doping concentration. Single crystals were mounted on carbon tape and evaluated using a Hitachi 3400N electron microscope equipped with an Oxford INCA EDX analyzer. An accelerating voltage of 15 kV was used, and the elemental analyses of five separate data points were averaged to obtain the approximate dopant concentration.

2.3. Spectroscopic Analysis.

Room temperature absorption spectra of $\text{Ln:Lu}_2\text{O}_3$ were obtained from single crystals that had been fabricated to an inspection polish using successive grinding by steel lapidary discs followed by 100,000 mesh diamond slurry. Polished samples were mounted in a custom-made aluminum alloy cryogenic cell with two fused silica windows capable of maintaining crystal temperatures between 298K and 80K to within $\pm 5^\circ$. The crystal in the cryogenic cell was kept under vacuum at less than 5×10^{-4} torr to help prevent condensation during cooling and subsequent warm-up of the apparatus. User-controlled flowing liquid nitrogen provided the cooling via a feed-through mounted underneath a copper sample holder equipped with a digital RTD sensor with a LakeShore Model 218 temperature monitor affixed near the sample. To

ensure good thermal conductivity, samples were securely held to the heat sink using indium foil and a spring loaded copper plate with 2 mm aperture. Absorption spectra were obtained on a Shimadzu SolidSpec-3700DUV instrument in transmittance mode. Scans were performed over the appropriate range using a resolution of 1 nm, scan speed of 1.67 nm/s and a sampling interval of 0.05 nm. Absorption spectra were corrected for Fresnel loss and baseline leveling and zeroing.

3. Results and Discussions

3.1. Phase Stability and Crystal Growth of $\text{Ln}:\text{Lu}_2\text{O}_3$.

The reaction products were initially evaluated from the hydrothermal reactions of Lu_2O_3 powder with the aqueous KOH mineralizer. These were performed at various temperatures to identify suitable conditions for prolonged growth of Lu_2O_3 crystals. Care must be taken with regard to the stability of other phases in the system, particularly $\text{Lu}(\text{OH})_3$ and $\text{LuO}(\text{OH})$. As in the $\text{Y}_2\text{O}_3\text{-H}_2\text{O}$ system [28], a transition from $\text{Lu}(\text{OH})_3$ to $\text{LuO}(\text{OH})$ appears to occur in aqueous solution around 425-450 °C. Of primary importance to us is a transition temperature from $\text{LuO}(\text{OH})$ to Lu_2O_3 , found to be around 600-620 °C. Neither transition appears to be a function of hydroxide concentration. We previously found that smaller crystals (< 2 mm per edge) of Lu_2O_3 could be obtained after 14 days at 620-640 °C, but these crystals would also become coated with $\text{LuO}(\text{OH})$ as the reaction cooled below 620 °C. Our interest in extending the study to higher temperatures was to determine whether the size of the crystals could be increased, and if the yield of the oxide material could be improved relative to any $\text{LuO}(\text{OH})$ material deposited during cool down. As expected, the oxide phase, Lu_2O_3 , was still observed to be the stable phase from 650-700 °C. Based on this stability, we targeted this higher-temperature regime for prolonged crystal growth to observe the effects of the new growth conditions.

Figure 1. Phase stability of the $\text{Lu}_2\text{O}_3\text{-H}_2\text{O-KOH}$ system under hydrothermal conditions. Dashed lines are provided to guide the reader to the approximate phase boundary temperatures.

The size of the Lu_2O_3 crystals formed in these higher temperature reactions increased significantly over those formed below 650 °C, and crystals up to 8 mm per edge were formed in the course of this study. Clearly there is sustained growth by transport processes to allow the nucleation sites to ripen to such sizes over a three week period. Furthermore, the thermal gradient across the reaction ampoules was more carefully controlled in the present study, and limited to 30 degrees or less. This has the important effect of minimizing nucleation sites so the as-grown material is concentrated on a few large crystals. Thus, experimental factors including increased solubility from the higher temperatures and suppressed nucleation from the narrow thermal gradient work in combination to produce larger crystals. In one particularly noteworthy instance, one single crystal with a mass of 1.75 g accounted for nearly 90% of the powdered feedstock (2 g) used in the reaction. It should also not be discounted that experiments performed in this higher temperature regime (650-700 °C) are further removed from the oxyhydroxide-oxide transition temperature (600-620 °C) than were previous experiments (600-650). Coupled with the narrow thermal gradient, the entire ampoule exists in the stability region for only Lu_2O_3 ,

whereas reactions performed below 650 °C were subject to areas of mixed LuO(OH)/Lu₂O₃ stability when the thermal gradient is considered. In general, less of the oxyhydroxide surface layer was observed to coat the bulk oxide crystals in the present studies, and in some instances the thin coating has been totally absent, revealing natural facets of the material (Figure 2). Improvements in optical clarity of the oxide were also observed, perhaps also due to the lower stability of the oxyhydroxide species under the present conditions.

Figure 2. Highly faceted, optically clear, as-grown Yb:Lu₂O₃ single crystal grown at 700 °C with a 30 degree thermal gradient. Crystal dimensions are 6 x 6 x 4 mm³.

The versatility of Lu₂O₃ as a host capable of accepting a wide range of lanthanide dopants was also studied. Previous work in our laboratory [22,24] focused on Yb³⁺ and Er³⁺ doping, in part because of their potential applications as laser crystals having 1 and 1.5 μm emissions, but also due to the size similarity between the host and dopant ions (Shannon crystal radii: Lu³⁺ = 1.001 Å; Yb³⁺ = 1.005 Å; Er³⁺ = 1.030 Å [29]). The question thus arises whether Lu₂O₃ will support the larger, lighter lanthanide elements as dopant ions. To test this, growth of Ln:Lu₂O₃ was performed for a much more comprehensive series of dopant ions (Ln³⁺ = Ce, Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, Tm, Yb) encompassing the full range of lanthanide crystal radii (Ce³⁺ = 1.15 Å; Yb³⁺ = 1.005 Å) [29]. A relatively high nominal dopant concentration of 5

at.% was chosen for these reactions to provide a rigorous test for dopant phase separation. For all these Ln:Lu₂O₃ reactions, only the lanthanide doped Lu₂O₃ was observed as a product and all trivalent lanthanides were found to enter the lutetia lattice (Figure 3). In general, there was not a significant size difference between doped and undoped Lu₂O₃ crystals in their as-grown form, and relatively large crystals were obtained for the entire range of earlier and later lanthanide dopant ions.

Figure 3: Hydrothermally-grown Ln:Lu₂O₃ crystals. Top row (from left): Ce:Lu₂O₃ (as grown, 2 mm), Pr:Lu₂O₃ (as grown, 7 mm), Nd:Lu₂O₃ (fabricated, 3 mm), Sm:Lu₂O₃ (as grown, 3 mm), Eu:Lu₂O₃ (fabricated, 3 mm), Tb:Lu₂O₃ (as grown, 3 mm). Bottom row (from left): Dy:Lu₂O₃ (fabricated, 3 mm), Ho:Lu₂O₃ (fabricated, 5 mm), Er:Lu₂O₃ (fabricated, 4 mm), Tm:Lu₂O₃ (as grown, 3 mm), Yb:Lu₂O₃ (as grown, 3 mm).

Evaluation of the dopant concentration in the as-grown crystals by EDX (and in some cases, spectroscopic means) showed excellent agreement between the concentrations in lattice with the nominal concentrations of dopant ions in the reaction charge for the smaller lanthanides (Eu-Yb). For Ce-Nd dopants, the dopant concentrations ranged from 1-2 at.% in the as-grown crystals using a 5 at.% reaction charge. So while there is some degree of dopant partitioning coefficient in these cases, it is clear that significant amounts of even the largest lanthanide ions can be doped in Lu₂O₃. For the early lanthanides, we attribute the lower dopant ion concentration in the lattice relative to the reaction charge to their larger size rather than any

solution solubility effects of the feedstocks. It should be noted that earlier attempts to prepare Nd:Sc₂O₃ single crystals resulted in complete separation of the Nd³⁺ dopant ion into a separate perovskite phase, NdScO₃, owing to the smaller size of the Sc³⁺ ion relative to Lu³⁺ [30]. The hydrothermal technique appears to be useful for obtaining relatively high dopant concentrations for a wide range of dopant ions in Lu₂O₃. Co-doping is also possible in Lu₂O₃, and large single crystals of several useful combinations of lanthanide dopants were obtained, including Yb:Tm:Lu₂O₃, Yb:Er:Lu₂O₃, and Yb:Ho:Lu₂O₃. Such doping schemes can introduce certain advantages in the resultant crystals via energy transfer processes, including more efficient or convenient optical pumping approaches, as well as the ability to study and utilize upconversion processes. Co-doped crystals were conveniently prepared by mixing the multiple dopant oxides with Lu₂O₃ in the feedstock for hydrothermal growth. In all these cases, hydrothermally-grown Lu₂O₃ appears to behave as a rather robust and versatile host material capable of accommodating a wide range of lanthanide ion sizes and concentrations.

3.2. Absorption Spectroscopy

A series of absorption spectra on the rare earth doped lutetia single crystals were obtained at both room temperature and cryogenic temperatures. In many cases these have been obtained for the first time. Most of these spectra will be discussed in considerably greater detail in subsequent publications. As an illustrative example of larger, early lanthanide dopant ions in Lu₂O₃, we show the absorption spectra of 1.2% Nd:Lu₂O₃ obtained at intervals from 298-80K (Figure 4). Typically we observe that the cryogenic spectra are exceptionally sharp and better resolved than the room temperature spectra, as would be expected. In some instances the cryogenic bands are narrower than the detector resolution, and we are in the process of

modifying the detector configuration to fully resolve these bands and obtain accurate cross section data. There is no significant change in the peak positions over the temperature range studied. Of particular interest for the 1.06 μm emission of Nd^{3+} is the $^4\text{I}_{9/2} \rightarrow ^4\text{F}_{5/2} + ^2\text{H}_{9/2}$ absorption transition. In $\text{Nd}:\text{Lu}_2\text{O}_3$ we find this absorption manifold to occur around 790-840 nm with especially strong absorption occurring at two wavelengths, 806 and 821 nm. This compares to Czochralski-grown $\text{Nd}:\text{YAG}$ and $\text{Nd}:\text{LuAG}$ having a single strongest absorption peak at 808-809 nm [31,32], and $\text{Nd}:\text{Y}_2\text{O}_3$ with two strong absorption peaks at 806 and 820 nm [33]. The absorption spectrum of $\text{Nd}:\text{Lu}_2\text{O}_3$ in the present study is also consistent with that reported from material grown by the floating zone method and used in preliminary laser demonstrations [34], further indicating the potential of the hydrothermal growth technique in the development of new optical materials.

Figure 4. Absorption coefficient of $\text{Nd}:\text{Lu}_2\text{O}_3$. Path length: 1.19 mm, resolution: 1 nm, scan speed: 1.67 nm/s, sampling interval: 0.05nm.

4. Conclusions

A modified approach to the hydrothermal growth of $\text{Ln}:\text{Lu}_2\text{O}_3$ has resulted in improvements in crystal size, yield, and optical clarity over previous studies. One of the key

parameters driving these improvements appears to be performing the hydrothermal reactions at somewhat higher temperatures (650-700 °C), where formation of LuO(OH) is not favorable. Application of a carefully-controlled thermal gradient was also beneficial in minimizing the number of nucleation sites, thereby concentrating the yield on only a few sites and improving the crystal size. Crystals up to 8 mm in size have been grown for multiple systems and growth of larger sized single crystals is underway. Despite the small size of the Lu³⁺ host ion, the present study found that all lanthanide ions of spectroscopic interest could be doped into the Lu₂O₃ lattice using this hydrothermal technique. Preliminary spectroscopic investigations display excellent resolution for all dopants with considerably greater detail observed at 80K. More detailed optical studies are in progress for several of these Ln:Lu₂O₃ systems, which hold promise in a variety of optical applications, and will be reported in due course.

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