Synthesis and Characterization of Erbium Lithium Niobium Gallium Garnet

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The synthesis of a new garnet, \(\text{Er}_3\text{Li}_{0.275}\text{Nb}_{0.275}\text{Ga}_{4.45}\text{O}_{12}\) (ErLNGG), by solid-state reaction, is reported. A comparison of the fluorescence spectra of Er\(^{3+}\) in ErLNGG, Er-doped (0.1 at.\%) calcium lithium niobium gallium garnet (CLNGG), and Er(50 at.\%):CLNGG is presented. The narrowing of luminescence lines suggests an ordering of the partially disordered CLNGG with the increase of erbium concentration.

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1. Introduction

At present, there is increasing interest in rare-earth-doped laser crystals with inhomogeneously-broadened optical spectra. The rare-earth-doped partially disordered garnets calcium niobium gallium garnet (CNGG) and calcium lithium niobium gallium garnet (CLNGG) are such crystals, having broad spectral bands and mechanical and thermal properties superior to glasses. Their wide absorption bands make them suitable active media for laser-diode-pumped solid-state lasers [1–3], while their wide emission bands can be used to obtain tunable solid-state lasers and ultrashort-pulse lasers [4–6].

Erbium-doped CNGG and CLNGG were studied for the possibility of improving the laser emission on transitions \(^{4}I_{11/2} \rightarrow ^{4}I_{15/2}\) and \(^{4}I_{13/2} \rightarrow ^{4}I_{15/2}\); to our knowledge, the investigation of the spectroscopic parameters of these crystals was limited up to now to low dopant concentrations [7, 8].

In this paper, the solubility limit of Er\(^{3+}\) in CLNGG is found to be 100 at.\%; this value is proved by the synthesis of the erbium lithium niobium gallium garnet (ErLNGG). The synthesized crystalline powder is investigated by X-ray diffraction and optical spectroscopy. The luminescence spectra of ErLNGG are compared with the spectra obtained in Er(0.1 at.\%):CLNGG and Er(50 at.\%):CLNGG.

2. Experimental

For the synthesis of the ErLNGG and Er:CLNGG, a solid-state reaction technique was used. A Nabertherm LHT 02/18 furnace was used for the thermal treatments. The X-ray diffraction analysis was performed using a Bruker diffractometer with Cu \(K_a\) radiation.

The luminescence spectra of the ErLNGG were obtained using a powder sample in a quartz cuvette; the powder was obtained by grinding the synthesized ceramic pellet in an agate mortar with pestle.

For the luminescence of Er(0.1\%):CLNGG, a bulk crystalline sample was used. The Er(50\%):CLNGG sample was also a powder synthesized by solid-state reaction and its luminescence was measured using a quartz cuvette.

The luminescence spectra on the transition \(^{4}S_{3/2}, ^{2}H_{2}(11/2) \rightarrow ^{4}I_{15/2}\) were excited in UV (wavelength range 300–400 nm) using a Xe–Hg arc lamp with a CuSO\(_4\) solution filter and a Schott UG1 glass filter. The luminescence was collected using a concave mirror and focused on the entrance slit of a Horiba Jobin-Yvon 1000M Series II monochromator. The detector was an EMI S-20 photomultiplier. For the recording of data we used a SR540 optical chopper and a SR830 lock-in amplifier from Stanford Research Systems.

An absorption spectrum of a bulk Er(5\%):CLNGG sample was recorded using a tungsten-halogen lamp included in a similar setup.

3. Results and discussion

The stoichiometric composition of the erbium lithium niobium gallium garnet was chosen to correspond to the optimum lithium content of CLNGG [9]: \(\text{Er}_3\text{Li}_{0.275}\text{Nb}_{0.275}\text{Ga}_{4.45}\text{O}_{12}\). For its synthesis, the following raw materials were used: Li\(_2\)CO\(_3\) (Serva International), Nb\(_2\)O\(_5\) (Johnson Matthey Chemicals Ltd., spectrographically standardized), Ga\(_2\)O\(_3\) (Alfa Aesar, 99.999\%), and Er\(_2\)O\(_3\) (Aldrich Chem. Co., 99.99\%\%). The raw materials were mixed in the right proportions and homogenized using an agate mortar and pestle. The mixture was then pressed in a pellet and kept for 15 h at 900\(^\circ\)C to
decompose the Li$_2$CO$_3$; afterwards, the pellet was ther-
mally treated for 36 h at 1300°C. A polycrystalline ce-
amic pellet was obtained. Polycrystalline CLNGG ce-
ramics were obtained by the same method, using CaCO$_3$
(Riedel–de Haën, precipitated, puriss.) instead of Er$_2$O$_3$.

For the synthesis of the Er:CLNGG crystals with con-
centrations 0.1% and 5%, the raw materials consisted of
CLNGG and ErLNGG, ground and mixed in the right
proportion. The mixture was homogenized using the
agate mortar and pressed in pellets. The pellets were
thermally treated for 36 h at 1300°C; after the treatment,
they were used for growing Er:CLNGG single crystals by
the Czochralski technique.

A similar method was used for the preparation of the
Er(50%):CLNGG sample; after the thermal treatment,
the resulting pellet was ground in the agate mortar.

The growth of the Er:CLNGG single crystals was per-
formed by pulling from the melt contained in a plat-
num crucible of 30 mm diameter and 30 mm height,
in air. The pulling rate was 2 mm/h at a rotation rate
of 20 rpm. The melting was done by induction heating
at 1450°C. The Er:CLNGG single crystals were grown
using a (111)-oriented seed obtained from a preliminary
platinum wire-grown crystal.

The X-ray diffraction pattern obtained for the
ErLNGG sample is presented in Fig. 1. It proves the
garnet structure of the sample and presents no lines cor-
responding to other crystalline phases. The main diffrac-
tion peaks are associated in Fig. 1 to their correspond-
ing Miller indices [10]. The lattice parameter was found
($a = 12.2514$ Å) at room temperature, smaller than the
lattice parameters found for CLNGG (12.51 Å) and
NLNGG (12.508 Å) [11]; this is in accord with the ionic
radius of Er$^{3+}$ being smaller than the ionic radii of Ca$^{2+}$
and Nd$^{3+}$ in dodecahedral coordination.

The luminescence spectra of the transition
($^4S_{3/2},^2H_{21/2} \rightarrow ^4I_{15/2}$) in Er:CLNGG samples of
erbium atomic concentrations 0.1%, 50% and 100% are
presented in Figs. 2 and 3. For the ease of comparison,
all spectra were normalized to their maximum and the
spectrum of the 50% sample is presented in both figures.
A decrease of the linewidths of the spectra is easily
observed with the increase of the erbium concentration,
denoting a decrease of the disorder of the neighborhood
of Er$^{3+}$. This trend is opposite to the evolution of the
linewidths with the increase of dopant concentration
observed in an ordered garnet (YAG) and described
in [12]. This can be explained if we take into account the
different nature of disorder treated in [12]. While in the
present work the disorder is an intrinsic characteristic of
the CLNGG lattice, in the Er:YAG crystals studied in
[12] the disorder is due to the random spatial distribution
of the dopant ions in the ordered host lattice.

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trend is noticed for all luminescence lines at wavelengths shorter than 550 nm. This phenomenon is due to the re-absorption of the luminescence of the $^{2}H_{21/2}$ level in the sample; re-absorption becomes stronger with the increase of Er$^{3+}$ concentration in the samples. To support this explanation, we present in Fig. 4 the absorption spectrum of a bulk Er(5%):CLNGG sample; this spectrum presents intense absorption lines at wavelengths up to 550 nm, in the same spectral range as the luminescence lines that decrease with the increase of Er$^{3+}$ concentration.

Fig. 4. Absorption spectrum of an Er(5%):CLNGG sample on transition $^{4}I_{15/2} \rightarrow (^{4}S_{3/2}, ^{2}H_{21/2})$. The horizontal axis limits were kept the same as in Figs. 2 and 3 for the ease of comparison. The vertical axis represents the absorption coefficient.

4. Conclusions

A new crystal, Er$_{1}$Li$_{0.275}$Nb$_{0.275}$Ga$_{4.45}$O$_{12}$, was synthesized by solid-state reaction. Its garnet structure was confirmed by X-ray powder diffraction analysis. Luminescence spectra obtained on transition $^{4}S_{3/2} \rightarrow ^{4}I_{15/2}$ of Er$^{3+}$ in samples of Er:CLNGG of various concentrations up to 100 at.% put into evidence a narrowing of the spectral lines with the increase of erbium concentration. This fact suggests an ordering of the partially disordered CLNGG with the increase of erbium concentration.

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References