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Far-infrared spectra of dysprosium doped yttrium aluminum garnet nanopowder

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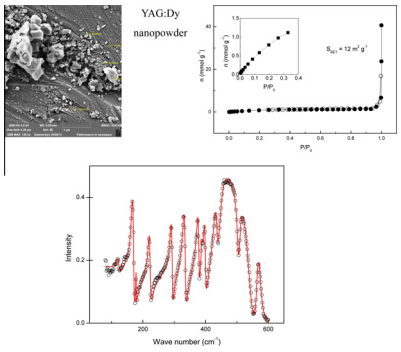
HIGHLIGHTS

- YAG:Dy nanopowder was produced by Solution Combustion Synthesis (SCS) method.
- Powders are composed by well-defined and separated nanoparticles.
- Some particles are agglomerated but there are also separated particles.
- The dielectric function was modeled by the Maxwell–Garnet formula.
- Optical phonon confinement is registered.

GRAPHICAL ABSTRACT



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ABSTRACT

The solution combustion synthesis was used to prepare nanopowders of yttrium aluminum garnet (YAG) and YAG doped with dysprosium ions, Dy^{3+}, (YAG:Dy). The morphology, specific surface area, texture, and optical properties of the prepared materials were studied by the means of scanning electron microscopy (SEM), nitrogen adsorption method, and far-infrared spectroscopy at room temperature in the spectral region between 80 and 600 cm^{-1}. It was established that all the examined samples were microporous. The Maxwell–Garnet formula was used to model dielectric function of YAG and YAG:Dy nanopowders as mixtures of homogenous spherical inclusions in air.

1. Introduction

Importance of yttrium aluminum garnet, $Y_3Al_5O_{12}$, commonly abbreviated as YAG, arises from its high chemical stability as well as excellent optical and high-temperature mechanical properties [1]. It is a ceramic material with a cubic garnet crystallographic structure whose thermal expansion is isotropic, whereas its optical properties are homogeneous, without birefringence effects [2,3]. Over the last five decades the structural properties of YAG were the subject of numerous studies, which proved its technological relevance and led to its use in a broad range of applications. For example, YAG has found its role as a host material in solid-state lasers of different kinds, luminescence materials, and scintillators [4–6].

Two prospective applications particularly draw attention toward trivalent dysprosium-activated optical materials. Namely,

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if the phonon energy of host matrix is low, these materials could be an alternative to praseodymium-doped optical amplifiers used in the second telecommunication window [7]. The second promising area of application, the solid-state lasers operating in the visible part of the spectrum [8], is based on the blue and yellow emissions originating from $^4F_{9/2}$ level of Dy^{3+}. These emissions are much more probable than the non-radiative relaxation to the next lower energy level, $^6F_{3/2}$, that corresponds to large energy gap of approximately 7500 cm^{-1}. Consequently, relatively high phonon energy of yttrium aluminum garnet presents YAG crystal as a prospective host material for dysprosium ions [9].

We used solution combustion synthesis (SCS) method to prepare nanopowder samples of YAG and YAG doped with 2 mol% Dy. Optical properties of the samples were analyzed by far-infrared spectroscopy (FIR), whereas nitrogen adsorption method was employed to examine specific surface area and texture. The dielectric function of the nanopowders was modeled using the Maxwell–Garnet formula.

2. Samples preparation and characterization

The SCS method used to prepare the YAG and YAG:Dy nanopowder samples was performed in several steps. Yttrium oxide (Y_2O_3) and aluminum oxide (Al_2O_3) of 99.99 % purity was purchased from the NOAH Technologies. The oxides were dissolved in HNO_3 followed by the addition of carbohydrazide to the solution of aluminum nitrate and yttrium nitrate:

$$3Y(NO_3)_3 + 5Al(NO_3)_3 + 15CH_6N_4O \rightarrow YAG + 42N_2 + 15CO_2 + 45H_2O.$$

Good reactivity of the raw materials provided absence of the intermediate phases, e.g., YAM ($Y_4Al_2O_9$) or YAP ($YAlO_3$), in the obtained YAG powder. The YAG:Dy samples were produced by doping YAG host with Dy^{3+} ions using the concentration of 2 mol %. Further, YAG:Dy nanopowder was annealed in the air atmosphere at 1300 °C with the aim to obtain full crystallinity [10].

The morphology of the prepared YAG and YAG:Dy nanopowders was examined using a high resolution scanning electron microscope (SEM) equipped with the high brightness Schottky Field Emission gun (FEGSEM, TESCAN) operating at 4 kV. In order to provide conductivity of the samples needed for SEM analysis, the samples were coated with gold/palladium. The SEM images of our YAG and YAG:Dy samples are given in Fig. 1. The powders are composed of well-defined and separated nanoparticles, clusters, and agglomerated particles. The size of individual spherical particles is in the range of about 30–50 nm. The spherical shape of particles is of great importance because it provides lower light scattering and brighter luminescence performance [11].

3. Results and discussion

3.1. Adsorption isotherms – BET experiments

The analyzer Surfer (Thermo Fisher Scientific, USA) was used to examine YAG and YAG:Dy nanopowders.

The dependences of the adsorbed amount of N_2 on the relative pressure, P/P_0, at the temperature of −196 °C, i.e., the nitrogen adsorption isotherms, for the YAG and YAG:Dy samples are given in Fig. 2. The adsorptions at low relative pressures, given in the graph inserts, indicate that there are micropores on the particle surfaces. According to the IUPAC classification pores are classified as macropores (pore width above 50 nm), mesopores (pore width 2–50 nm) and micropores (pore width below 2 nm) [12]. At the same time, non-limiting adsorption at high P/P_0, was found to correspond to non-rigid aggregates of particles giving rise to slit-shaped pores [13]. Note that these conclusions are in agreement with the SEM images given in Fig. 1, which show that our samples contain agglomerated as well as separated particles. The separated particles are found to be spherical with the diameter of approximately 40 nm. The specific surface areas calculated by the BET equation, S_{BET}, are found to be 5 $m^2\,g^{-1}$ and 12 $m^2\,g^{-1}$ for the YAG and YAG:Dy samples, respectively. Since the radius of Dy^{3+} ion of 0.1167 nm is larger than the radius of Y^{3+} ion, which is 0.1159 nm, it comes as no surprise that the presence of Dy led to increase of the overall specific surface of particles. Also, dopants introduce defects into the structure of the material which results in different charge on the particle surface when doped and undoped are compared. This charge on the particle surface leads to differences in packaging particles and their greater or lesser agglomeration, which on the other hand have significant role on the porosity and specific surface area. Incorporated dopants have a tendency to concentrate at the surface of nanomaterials. All these have significant role on the increasing of the specific surface area.

3.2. Far-infrared spectroscopy

The far-infrared measurements were carried out with the BOMEM DA – 8 FIR spectrometer. The wave number range between 80 and 600 cm^{-1} was covered with the DTGS pyroelectric detector.

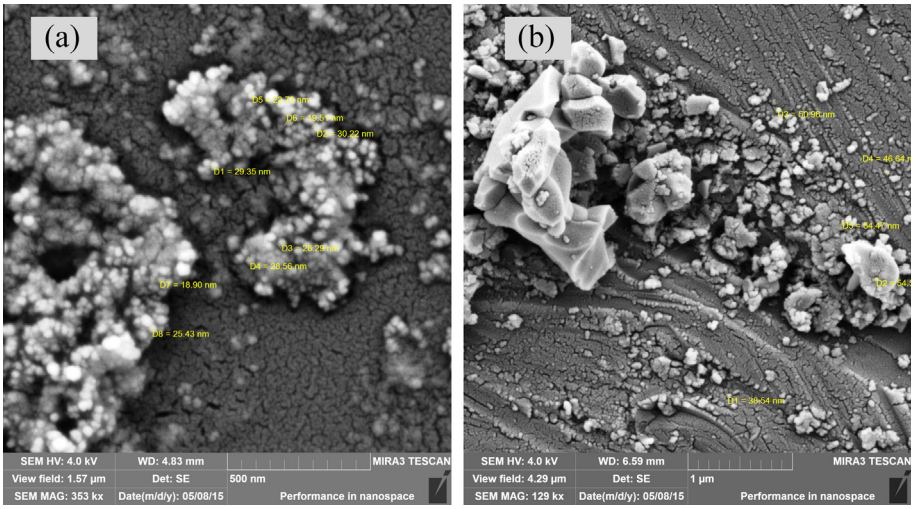

Fig. 1. SEM micrographs. The micrographs of YAG and YAG:Dy nanopowders are given in part (a) and (b), respectively.