Letter

Laser synthesis of ruby and its nanoparticles for photo-conversion of solar spectrum

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Received 3 November 2022
Accepted for publication 26 January 2023
Published 14 February 2023

Abstract
Ruby grains are synthesized by laser heating of the dry mixture of Al₂O₃ and Cr₂O₃ in air. Quasi-continuous radiation of a Nd:YAG laser was used for this purpose with an average power of 15 W. The synthesized ruby was characterized by x-ray diffractometry. Ruby grains demonstrate strong photo-luminescence in the vicinity of 700 nm. Ruby particles were further fragmented to smaller particles using the technique of laser fragmentation in liquids and integrated into a polymer matrix. A luminescence map acquired with the help of a photo-fluorimeter confirms efficient photo-conversion of green-blue radiation of the synthesized ruby into the red region.

Keywords: laser synthesis, ruby, nanoparticles, luminescence, photo-conversion, green houses

(Some figures may appear in colour only in the online journal)

1. Introduction
Solar radiation is a black body radiation with a maximum at the wavelength of 555 nm. This radiation is used by plants for photosynthesis. However, some parts are of high importance for various stages of proliferation. The most demanded radiation for efficient proliferation of land plants is in the red range of the spectrum around 700 nm and longer [1]. Also, the radiation around 400 nm is also important in another cycle of proliferation. This is especially true for land plants grown in green houses in the terrestrial areas of risky agriculture [2, 3]. However, the fraction of radiation in this range in the solar spectrum is rather small. Therefore, the photo-conversion of solar radiation to the red region is highly desirable.

Significant efforts were applied for photo-conversion of the solar spectrum to the red region. Semiconductor-based coatings, such as CdS or CdSe could be a possibility to create the coatings that convert solar radiation to the red region. However, these coatings are not stable under solar light and degrade in a short time. Same concerns are that the coatings based on organic dyes are not photostable. Ruby may be an alternative to semiconductors. Ruby has an Al₂O₃ lattice in which some Al³⁺ ions are substituted by Cr³⁺ ions. Ruby is highly photo-stable and is characterized by strong photoluminescence (PL) in the vicinity of 695 nm [4]. The first laser was realized just on the ruby crystal. This wavelength is of high interest for use in green house coatings.

Direct laser synthesis of ruby had already been realized by laser exposure of the mixture of Al₂O₃ with Cr₂O₃ [5, 6]. The authors used in their work a continuous wave Nd:YAG laser with wavelength of 1064 nm and average power of order of 100 W scanned across the mixture surface. The synthesized ruby crystals were thoroughly characterized by x-ray diffraction technique, scanning electron microscopy and...
electron paramagnetic resonance technique. Infrared characterization of the obtained ruby was also performed. However, visible luminescence of the synthesized ruby crystals was not explored. Nanoparticles of ruby can be obtained by laser ablation of ruby crystals in liquids [7, 8]. In this case, however, the Cr$^{3+}$ content in these nanoparticles is determined by the composition of initial target material. The most available ruby crystals are bulk laser ruby crystals containing Cr$^{3+}$ at the concentration of 0.05%. For applications as photo-converse coatings the concentration should be higher in order to compensate for the small size of used ruby particles. Therefore, direct laser synthesis of ruby is a preferable way for obtaining ruby particles with desired Cr$^{3+}$ content [9]. The main emphasis of the present work is given to the spectrum of PL of synthesized ruby particles at various Cr$^{3+}$ content under excitation with various wavelengths.

2. Methodology

In this work ruby particles at various Cr$^{3+}$ content were obtained by laser heating of mixture of industrial Al$_2$O$_3$ and Cr$_2$O$_3$ micro-powders in air. A layout of the experimental setup for obtaining ruby grains is shown in figure 1.

First, the mixture of industrial Al$_2$O$_3$ micro-powder with Cr$_2$O$_3$ micro-powder was prepared with Cr$^{3+}$ content 2, 5, or 8%. The mixture was placed on the bottom of alumina crucible. The thickness of the mixture layer was about 2 mm. The crucible was covered by a soda-lime glass plate. The mixture was exposed to quasi-continuous wave radiation of a Nd:YAG laser with wavelength of 1064 nm in air modulated at frequency of 200 kHz by 1.5 µs pulses with depth of modulation about 30%. The glass cover was far enough in distance above the irradiated layer to avoid its cracking due to overheating. A laser beam was scanned across the surface of the layer with the help of F-theta objective ($F = 93$ mm) and galvo-controlled system of two mirrors. The estimated diameter of the laser spot was 100 µm, scanning velocity of the beam was 100 mm s$^{-1}$. Average power of the laser radiation was 15 W, which corresponds to a power density of 150 kW cm$^{-2}$ on the surface of the mixture. Both components of the mixture are almost transparent at laser wavelength at low intensity of radiation, so the absorption depth is comparable with the thickness of the mixture. The mass of the mixture exposed to laser radiation was around 1 g. The scanning is accompanied by bright heat emission from the laser-exposed mixture. The mixture was mechanically mixed again after scanning and subjected to another cycle of laser irradiation in the direction perpendicular to the first scanning. The duration of the scanning cycle was about 4 min.

The procedure of laser fragmentation of synthesized ruby grains was applied to reduce their size. Schematic of the experiment on fragmentation of ruby particles is shown in figure 2. Laser fragmentation is a well-established process. It consists of a laser exposure of suspension of either micro- or nanoparticles in a liquid [10–13]. The laser beam is focused inside the suspension. The synthesized ruby grains were subjected to laser fragmentation in isopropanol. The choice of such a liquid was due to its anhydrous composition. In the first experiments, it was found that fragmentation in H$_2$O is accompanied by the formation of aluminum hydroxide during laser irradiation of ruby grains. The same laser was used for fragmentation. Laser parameters were as follows: Q-switch mode, the repetition rate of laser pulses of 10 kHz, pulse duration of 10 ns and the energy per pulse of 2 mJ. The size of ruby grains is fairly large, so the suspension was stirred with the help of rotating glass
3. Results and discussion

Macro-view of ruby grains is shown in figure 3. One can see in figure 3 that agglomerates of ruby are made of spherical particles. This fact suggests that the synthesis of ruby proceeded via melting of the mixture of Al₂O₃ and Cr₂O₃ and exceeded 2400 °C (melting temperature of Cr₂O₃).

PL spectra of synthesized ruby particles excited at a wavelength of 405 nm were measured using an Ocean Optics spectrometer. The luminescence map of the polymer with impregnated ruby nanoparticles was measured with the help of spectro-fluorimeter Jasco FP-8300. In this fluorimeter the excitation of luminescence in a sample can be varied in wide spectral range from UV to infrared region. The diffraction patterns were recorded on a Bruker D8 Discover A25 DaVinci Design x-ray diffractometer. The size distribution function of nanoparticles after laser fragmentation was studied by dynamic light scattering (DLS) using Zetasizer ULTRA Red Label (Malvern Panalytical Ltd, Malvern, UK) operating at a wavelength of the laser radiation 632.8 nm.

Laser-fragmented nanoparticles of ruby were incorporated into a free-standing film of fluoropolymer LF-32. This type of polymer is widely used for green house coatings. A PL map of the nano-composite of fluoropolymer LF-32 with nanoparticles of ruby was acquired with the excitation wavelength varied from 300 to 650 nm. The luminescence map of the pure fluoropolymer is presented in figure 8(a), while luminescence map of the nano-composite in figure 8(b). One can see that the pure LF-32 shows the luminescence in the range 350–500 nm under excitation wavelengths 300–400 nm. Luminescence of the nano-composite comprised both PL peaks of LF-32 and PL peaks of ruby in the vicinity of 700 nm.

The nature of coupling of laser radiation with a wavelength of 1064 nm to the mixture of oxides used here for synthesis of ruby is worth discussion. The bandwidth of Al₂O₃ is around 6 eV, while for Cr₂O₃ it amounts to 3.1–3.4 eV according to different references. Therefore, both oxides are transparent at wavelength of 1064 nm. However, Cr₂O₃ has pronounced green color, which implies the absorption of red radiation with photon energies around 1 eV. Available to authors data sources do not contain any information of the origin of this absorption. One may suggest that this coloration may be ascribed to the transition from intrinsic doping levels in the gap of Cr₂O₃ to conduction band. These levels are thermally excited upon laser heating at elevated temperature. Therefore, the absorption of radiation at wavelength of 1064 nm by the mixture of oxides has a non-linear nature and increases with the increase of laser intensity. In other words, Cr₂O₃ is a thermal sensibilizer in the mixture of oxides used in this work.
Figure 4. Photoluminescence spectra of synthesized ruby under excitation by a laser radiation at wavelength of 405 nm. Cr\(^{3+}\) content is 2 (black) and 5% (red).

Figure 5. Diffractograms of initial alumina and of ruby with various Cr\(^{3+}\) content.
Figure 6. DLS size distribution of the ruby nanoparticles after laser fragmentation in isopropanol for 45 min.

Figure 7. Photoluminescence spectrum of laser-fragmented ruby grains in isopropanol under excitation by a laser radiation at wavelength of 405 nm. Fragmentation time was of 45 min.
Figure 8. Luminescence map of ruby nanoparticles in fluoropolymer matrix. Luminescence of the fluoropolymer LF-32 (a) and fluoropolymer LF-32 doped with nanoparticles of ruby (b).
4. Conclusions

Thus, a simple and cost-efficient way of obtaining photoconversion coatings for green houses on the basis of ruby particles has been demonstrated. The synthesized ruby powder shows very efficient conversion of solar radiation in the blue-green region of the spectrum to required for the red region of PL. The cost of initial reagents, such as Al$_2$O$_3$ and Cr$_2$O$_3$ is low, and the energy of the laser consumed during the synthesis is in the easily affordable range. The obtained particles are highly photo-stable as stable is ruby in ruby lasers. A nano-composite of fluoropolymer with nanoparticles of ruby shows the PL peaks both in the vicinity of 700 nm and around 400 nm, which is favorable for the use of such material for green house coatings.

Acknowledgments

This work was supported by a grant of the Ministry of Science and Higher Education of the Russian Federation (075-15-2022-315) for the organization and development of a World-class research center ‘Photonics’. The authors thank the Common use center of GPI for X-ray diffractometry. The authors thank I V Baymler for his help in data curation.

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