

Growth of Yb:Na₂SO₄ crystals and study of their spectral–luminescent characteristics

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Abstract. Ytterbium-doped single crystals of the high-temperature hexagonal sodium sulphate modification are grown by the Czochralski method. It is found by energy dispersive analysis that the crystallisation occurs congruently. The Yb:Na₂SO₄ crystals have additional (with respect to Yb³⁺ ions) absorption bands in the regions of 650, 850 and 1150 nm, which obviously belong to colour centres. The luminescence spectrum of the Yb:Na₂SO₄ single crystal noticeably differs from the luminescence spectrum of Yb:YAG crystals by the presence of a broad band without a prominent peak. The luminescence decay curve for the powder is single-exponential with a time constant of 1175 μs, which is somewhat larger than that for the Yb:YAG crystal. The lifetime of the ytterbium excited state does not change during storage of the samples in air for a week.

Keywords: sodium sulphate, heterovalent isomorphism, ytterbium, luminescence spectra, crystal growth.

1. Introduction

The Na₂SO₄ compound is characterised by the existence of several phase transitions [1–3]. The hexagonal Na₂SO₄-I modification, which is isostructural to α-K₂SO₄ (space group *P*_{6₃}/*mmc*) is stable in the temperature range from 240 °C to the melting temperature (885 °C). The polymorphism of Na₂SO₄ makes it difficult to grow this single crystal from melt, because of which it is unknown among photonics materials. However, it is known that introduction of heterovalent additives, such as sulphates of di- and trivalent metals, into sodium sulphate provides the possibility to stabilise the high-temperature modification of Na₂SO₄ and make it stable at room temperature [1, 4–6]. According to the studied phase diagrams of the Na₂SO₄–R₂(SO₄)₃ system [5], it is this situation that is realised in systems of sodium sulphate with sulphates of rare-earth elements. In particular, introduction of neodymium sulphate allowed one to grow Nd:Na₂SO₄ single crystal for investigating cationic conductivity [7].

In the present paper, we describe sodium sulphate single crystals doped with ytterbium sulphate, which were grown in order to extend the range of crystals for near-IR lasers, and

study their spectral–luminescent characteristics. The choice of ytterbium as a dopant is explained by the lowest quantum defect in the case of diode pumping [8–10].

2. Experimental

As the initial charge for growing Yb:Na₂SO₄ single crystals, we used a mechanical mixture of sodium sulphate and ytterbium sulphate (3.5 mol %) synthesised at the Prokhorov General Physics Institute, Russian Academy of Sciences. The single crystals were grown by the Czochralski method in a ‘Kristal-2’ crystal growth furnace in platinum–rhodium crucibles with induction heating. Platinum wire was used as a seed. The nominal growth rate was 1 mm h^{−1} with a rotation rate of 6 rpm. After completing the crystal growth process and pulling the crystal away from the melt, the crystal was cooled to room temperature with a rate of 8 K h^{−1} to avoid a thermal shock. A photograph of the cleaved crystal is given in Fig. 1.

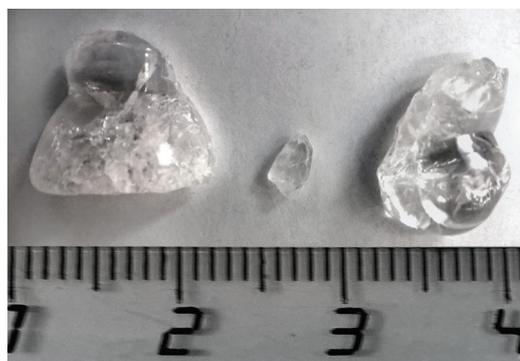


Figure 1. Photograph of an Yb:Na₂SO₄ single crystal.

Part of the single crystal was milled into powder and studied by powder X-ray diffraction with a Bruker D8 Advance diffractometer with the Cu K_α wavelength (Fig. 2). X-ray diffraction analysis allowed us to assign the grown single crystal to the high-temperature hexagonal Na₂SO₄-I modification (space group *P*_{6₃}/*mmc*). The calculated lattice parameters $a = 5.339(1)$ Å and $c = 7.157(4)$ Å are smaller than the corresponding parameters of pure sodium sulphate (JCPDS card #86-0800, $a = 5.393$ Å, $c = 7.246$ Å), which indicates that ytterbium enters the crystal with the formation of a solid solution.

The crystal composition was determined by energy dispersive analysis using a Carl Zeiss NVision 40 microscope with

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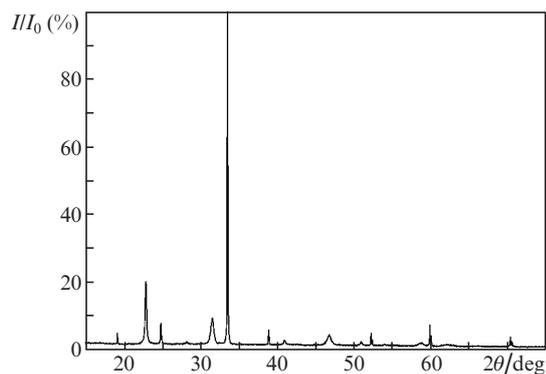


Figure 2. X-ray diffraction pattern of Yb:Na₂SO₄ powder.

an energy dispersive spectrometer. The determined composition of the Na₂SO₄ crystal doped with ytterbium (3.8 mol %) corresponded to its nominal composition (3.5 mol %) within the measurement error, which testifies to the congruent crystallisation of the melt.

The spectral–luminescent characteristics were studied in unpolarised light because additional orientation and polishing of the samples at room temperature might lead to their degradation with the formation of Na₂SO₄·10H₂O crystal hydrate. The transmission spectra were studied using a Shimadzu UV-3101PC spectrophotometer with a slit width of 1 nm and correction for reflection losses. The transmission spectrum of the Yb:Na₂SO₄ crystal 2.6 mm thick is presented in Fig. 3 in comparison with the transmission spectrum of an Yb:YAG crystal with an ytterbium concentration of 10 at % and a thickness of 0.92 mm (Research Institute of Materials Science). One can see that the Yb:Na₂SO₄ crystal have additional (with respect to Yb³⁺) absorption bands in the regions of 650, 850 and 1150 nm. These bands, as well as the increased absorption in the UV spectral region, are probably related to colour centres.

The transmission spectrum of the Yb:Na₂SO₄ crystal in the region of Yb³⁺ absorption in comparison with the spectrum of the Yb:YAG crystal is shown in Fig. 4. One can see that the absorption spectrum of trivalent ytterbium in the Yb:Na₂SO₄ crystal has a less pronounced structure than the Yb³⁺ spectrum in yttrium aluminium garnet.

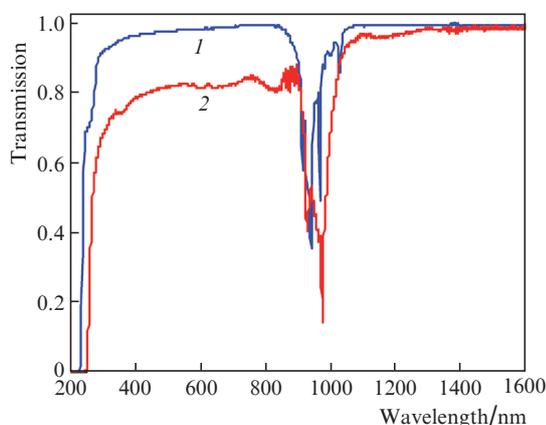


Figure 3. Transmission spectra of (1) Yb:YAG and (2) Yb:Na₂SO₄ crystals.

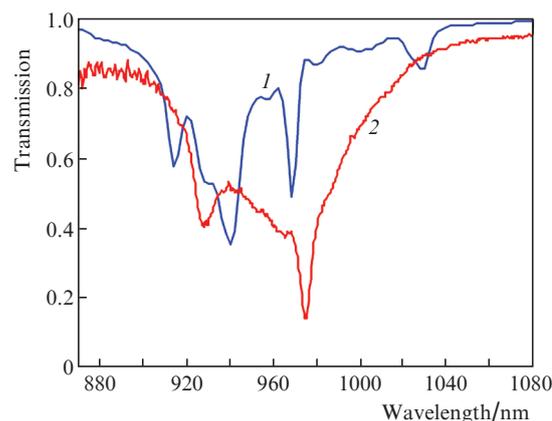


Figure 4. Transmission spectra of (1) Yb:YAG and (2) Yb:Na₂SO₄ crystals in the region of Yb³⁺ absorption.

The luminescence spectra of Yb:Na₂SO₄ and Yb:YAG crystals were studied at room temperature using an InSpectrum INS-250 spectrometer (Roper Scientific Acton Research Corp.) (Fig. 5). The narrow line at a wavelength of ~963 nm for the Yb:Na₂SO₄ single crystal is formed by the scattered radiation of the pump laser diode. The luminescence spectrum of the Yb:Na₂SO₄ sample considerably differs from the luminescence spectrum of Yb:YAG. The luminescence bands of Yb:Na₂SO₄ are broadened, and the spectrum consists of a broad band without a pronounced peak.

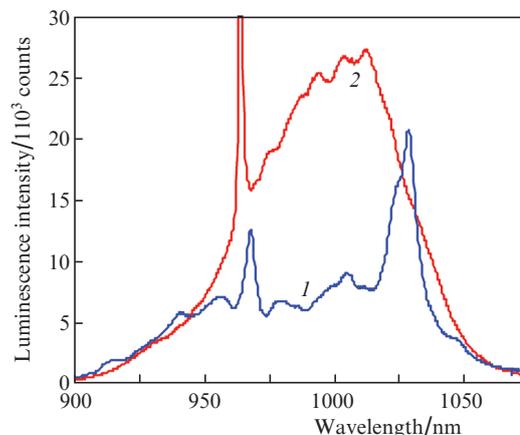


Figure 5. Luminescence spectra of Yb³⁺ ions in (1) Yb:YAG and (2) Yb:Na₂SO₄ crystals.

The luminescence lifetime of the Yb:Na₂SO₄ single crystal and its powder was measured using an FD-7G germanium photodiode under excitation by laser diode pulses with a duration of 1 ms (Fig. 6). The time constant of the recording system was ~3 μs. Analysis of the luminescence decay curves revealed reabsorption even in small crystals [curve (1) in Fig. 6], which leads to an increase in the apparent decay time (to 1556 μs) and to the appearance of a slow decay component with a different time constant. We managed to measure the real lifetime for a powder milled from the single crystal. The decay curve for the powder is determined by a single exponent with a time constant of 1175 μs, which is somewhat larger than for the Yb:YAG crystal (950–1000 μs [11, 12]).

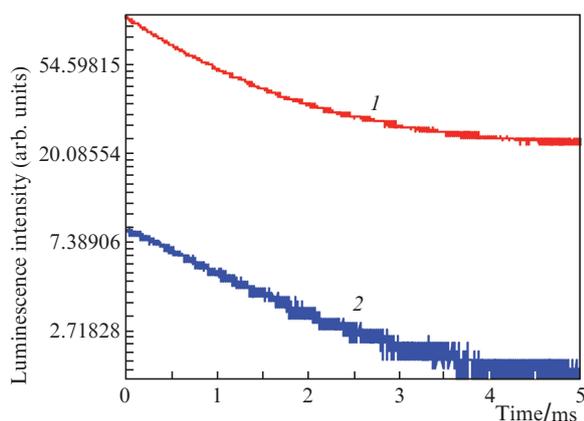


Figure 6. Luminescence decay curves of (1) an $\text{Yb}:\text{Na}_2\text{SO}_4$ crystal with a volume of 1.5 mm^3 and (2) $\text{Yb}:\text{Na}_2\text{SO}_4$ powder with a grain size smaller than 0.1 mm .

3. Discussion of results

Stabilisation of high-temperature modifications by iso- and heterovalent substitutions is a well-known physicochemical method [13]. This method was previously demonstrated for the $\alpha\text{-YF}_3$ structure, which is typical for non-quenchable high-temperature modifications of trifluorides of rare-earth elements of the yttrium subgroup. This phase was stabilised by adding scandium, magnesium and manganese fluorides [14, 15]. A similar example is the stabilisation of the high-temperature cubic zirconia modification by rare-earth solid solutions with formation of solid solutions, which gave rise to the fianite family [16]. The high-temperature hexagonal gadolinium fluoride modification can be stabilised by introduction of calcium or strontium fluorides [17, 18], while additional doping with Nd^{3+} ions allowed one to obtain laser media [19].

Anhydrous Na_2SO_4 is stable at temperatures above 32.4°C , while $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ crystal hydrate is formed below this temperature in the presence of water. The doped crystals synthesised in the present work are rather stable in atmospheric air, since the luminescence spectra and the excited state lifetime for the powder did not change during storage in air for a week.

The observed character of the absorption and luminescence spectra can be explained by the conditions of entering of Yb^{3+} ions into the Na_2SO_4 crystal. The ionic radii of Yb^{3+} and Na^+ differ by less than 10% [20], because of which the substitution of Na^+ ions by Yb^{3+} is quite possible. However, the difference in the valences of the cations requires charge compensation. Heterovalent substitution in solid solutions based on the high-temperature Na_2SO_4 modification occurs with the formation of vacancies in the cationic sublattice [1]. Correspondingly, ytterbium ions enter the synthesised crystal according to the scheme $3\text{Na}^+ \rightarrow \text{Yb}^{3+} + 2\text{V}_{\text{Na}}$. This leads to ambiguity in the nearest surrounding of Yb^{3+} ions, which causes inhomogeneous broadening of the absorption and luminescence lines.

4. Conclusions

Ytterbium-doped single crystals of the high-temperature hexagonal sodium sulphate modification are grown by the Czochralski method, and it is shown that the crystallisation occurs congruently. The $\text{Yb}:\text{Na}_2\text{SO}_4$ single crystals have

additional (with respect to Yb^{3+} ions) absorption bands in the regions of 650, 850 and 1150 nm, which are obviously related to colour centres. The luminescence spectrum of the $\text{Yb}:\text{Na}_2\text{SO}_4$ single crystal exhibits broadening of luminescence lines into a broad band without a pronounced peak. The changes in the absorption and luminescence spectra are explained by the conditions of entering of ytterbium into the crystallographic position of sodium, which leads to the formation of two sodium vacancies. The luminescence decay curve of $\text{Yb}:\text{Na}_2\text{SO}_4$ powder is determined by a single exponent with a time constant of $1175 \mu\text{s}$, which does not change during storage of samples in air for a week.

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