Cryst. Res. Technol.	36	2001	11	1223–1229

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Optical and Luminescence Properties of $YAlO_3$-Tm Crystals

The results on optical absorption, photoluminescence and thermoluminescence of YAP-Tm crystals of 1 at.% and 4 at.% of Tm are presented as well as influence of UV-, γ-radiation and thermal treatments on optical and luminescence properties of the crystals. The blue-green luminescence of defect centers was observed in YAP-Tm crystals at Ar^+-laser excitation. The possibility of energy transfer processes between defect centers and Tm^{3+} ions was shown.

Keywords: $YAlO_3$-Tm, optical absorption, luminescence, color centers

(Received March 2, 2001; Accepted July 2, 2001)

1. Introduction

Yttrium aluminum perovskite crystals $YAlO_3$ doped with thulium (YAP-Tm) in recent years are of interest as materials for 2 μm lasers at 4-5 at.% concentration of thulium and up-conversion visible lasers at ~1 at.% of thulium (ELDER et al., 1996; ELDER et al., 1998; GUY et al., 1998).

Though YAP-Tm crystals are of much interest, the problem of obtaining of large, structurally perfect and optically qualitative (free from cloudiness and parasitic absorption) crystals is not solved finally. The influence of point defects on YAP-Tm optical properties remains scanty studied. The purpose of the paper is investigation of influence of UV-, γ-radiation and thermal treatments on optical and luminescence properties of YAP-Tm crystals.

2. Experimental procedure

The YAP-Tm crystals were grown by the Czochralski technique with an automatic diameter control and radio frequency induction heating from iridium crucibles in argon atmosphere. The crystals were pulled in the [010] direction in Pbnm setting. The YAP-Tm (4 at.%) crystals (50 mm in diameter and more than 100 mm in length) and YAP-Tm (1 at.%) crystals (25×50 mm) were grown by the technologies described in detail by SAVITSKII et al., 2000 and NEUROTH et al., 1999 respectively.

The optical transmission spectra of investigated crystals were measured in visible and IR region at room temperature using UV-VIS LAMBDA 2, BECKMAN ACTA MVII, FT-IR

1705 and SPECORD M40 spectrophotometers. Spectra of additional absorption (AA) induced by external influence (irradiation, thermal treatment) were determined as difference between the optical absorption before and after external influence respectively.

Gamma-irradiation was performed using ^{60}Co source (the average energy 1.25 MeV) up to absorbed doses ~10^6 Gy. UV-illumination was performed using Ar^+-laser. Thermal treatments were done in air and hydrogen at T~ 1300 K.

Photoluminescence spectra were measured using GDM-1000 monochromator at Ar^+-laser excitation in 10-300 K temperature region. For recording of excitation spectra of photoluminescence the xenon lamp light was passed through M-31 monochromator.

Thermal glow and thermoluminescence spectra were measured after xenon lamp excitation at 10 K and successive heating up to room temperature. Thermal glow intensity was registered using photomultiplier with S-20 photocathode. Thermoluminescence spectra were recorded using CCD-camera with TRIAX 320 monochromator.

3. Results and discussion

The optical transmission spectra of YAP-Tm crystals are presented in Fig.1. Designation of thulium multiplets is also presented in Fig. 1. These results are in consistent with earlier published data (MANAA et al., 1994). For as-grown YAP-Tm (4 %) crystal besides Tm^{3+} absorption the wide absorption bands in UV and visible are observed. Similar absorption of defect centers are observed also in other YAP crystals (SUGAK et al., 1997). The main reasons of crystal coloration maybe a deviation from the stoichiometric composition (crystals are enriched with rare-earth ions) and recharging of uncontrolled metal impurities of iron group (SUGAK et al., 2001).

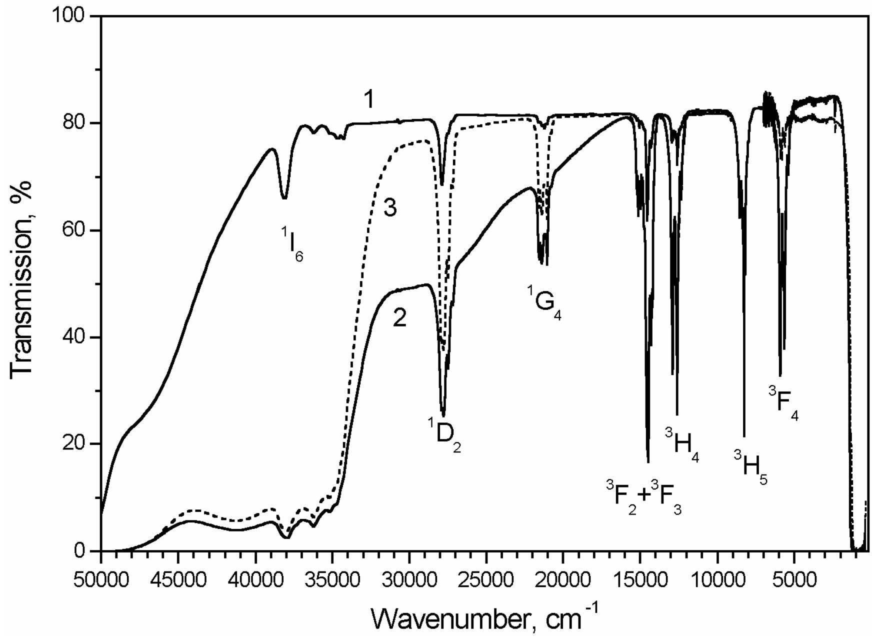

Fig. 1: The optical transmission spectra of YAP-Tm (1 %) as-grown (1); YAP-Tm (4 %) as-grown (2) and YAP-Tm (4 %) H_2-annealed (3) crystals.

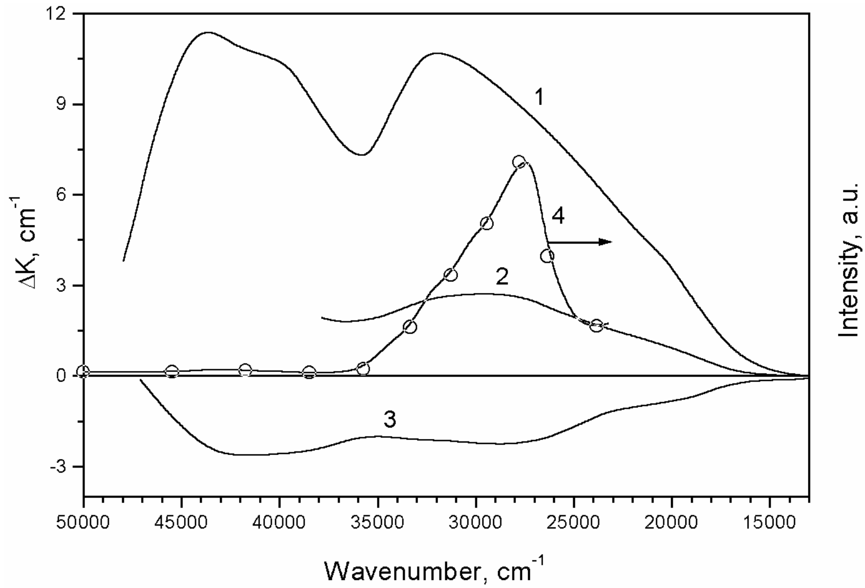

Fig. 2: The AA spectra of YAP-Tm (4 %): 1 – after gamma-irradiation; 2 – after UV-exposing; 3 – after H_2-annealing. 4 – The excitation spectrum of green luminescence (~20500 cm^{-1}) for YAP-Tm (1 %).

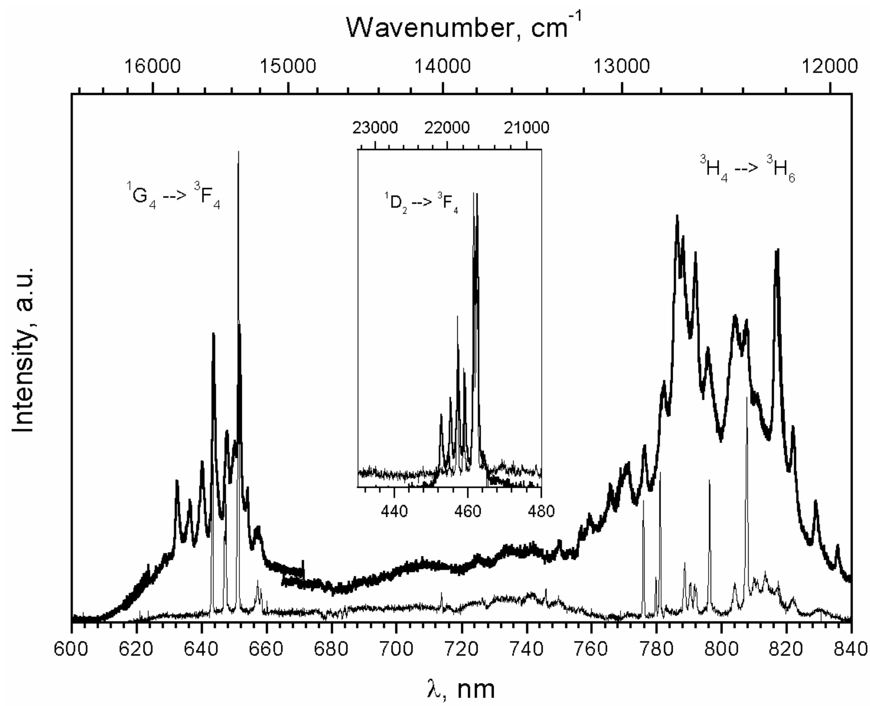

Fig. 3: The luminescence spectra of YAP-Tm (4%) at 450 nm (22200 cm^{-1}) and 370 nm (27000 cm^{-1}) excitation. Thin curve represents the luminescence spectrum at 10 K and thick one at 300 K.

Annealing of crystals in reducing atmosphere leads to a betterment of crystal optical transmission; air annealing, UV- or γ-irradiation conversely induces the additional absorption appearance. The AA spectra of YAP-Tm (4 %) are presented in Fig. 2. The induced absorption is caused by recharging of crystal growth defects (AKKERMAN et al., 1992; SUGAK et al., 2001). In the YAP-Tm (1 %) crystal the induced changes of optical absorption are by order of magnitude smaller due to smaller growth coloration of the crystal.

The photoluminescence spectra of YAP-Tm (4%) and YAP-Tm (1%) are mainly conditioned by transitions in Tm^{3+} ions. With a temperature decreasing the luminescence intensity of Tm^{3+} increases and becomes more precise. The luminescence spectra and designation of transitions are presented in Fig. 3.

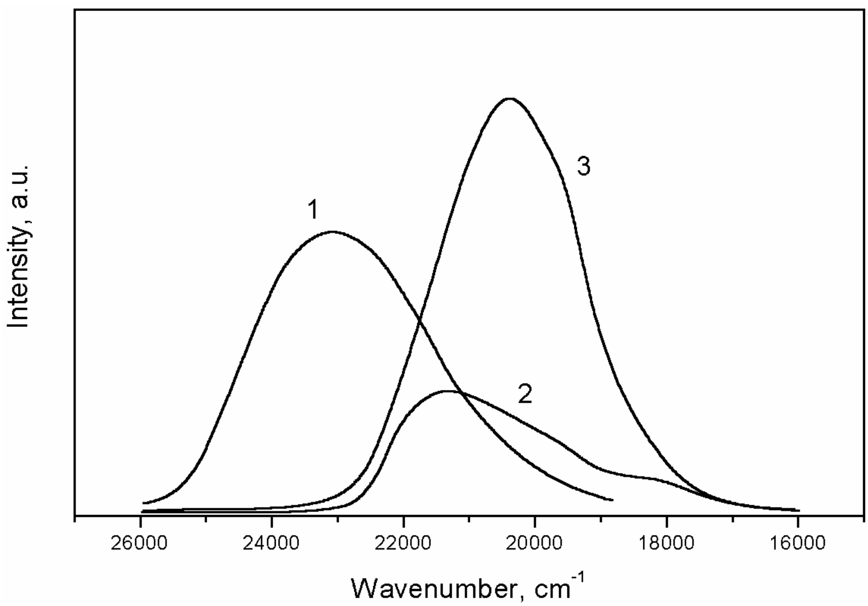

Fig. 4: The blue-green luminescence of defect centers in YAP-Tm (4 %) (1 – as-grown crystal; 2 – H_2-annealed) and YAP-Tm (1 %) as-grown (3) at 270 nm (37000 cm^{-1}) excitation at 300 K.

Except the luminescence of Tm^{3+} ions the wide and complex luminescence band in blue-green region is observed in both YAP-Tm (4%) and YAP-Tm (1%) crystals (Fig. 4). The luminescence maximum lie near 23000 cm^{-1} for YAP-Tm (4%) and 20500 cm^{-1} for YAP-Tm (1%). At that the luminescence intensity for YAP-Tm (1%) is higher. The excitation spectrum of blue-green luminescence for YAP-Tm (1%) represents a wide band in the 25000-35000 cm^{-1} region (Fig. 2, curve 4). As it is shown from Fig.2, the band 25000-35000 cm^{-1} is present in AA spectra induced by external influences, and is attributed to O^- centers in YAP crystals (AKKERMAN et al., 1992). One more reason that allow to attribute the blue-green luminescence to defect centers is a decreasing of the luminescence in crystals preliminary annealed in reducing atmosphere as well as decreasing of defects absorption in reduced crystals. The luminescence of defect centers near 20000 cm^{-1} and 16400 cm^{-1} in γ-irradiated YAP crystals was observed by ARSENEV et al., 1974. The luminescence near 16600 cm^{-1} and 15000 cm^{-1} in YAP crystals was observed by BARYSHEVSKY et al., 1993 and as well as luminescence observed by ARSENEV et al., 1974 was attributed to F-type centers.

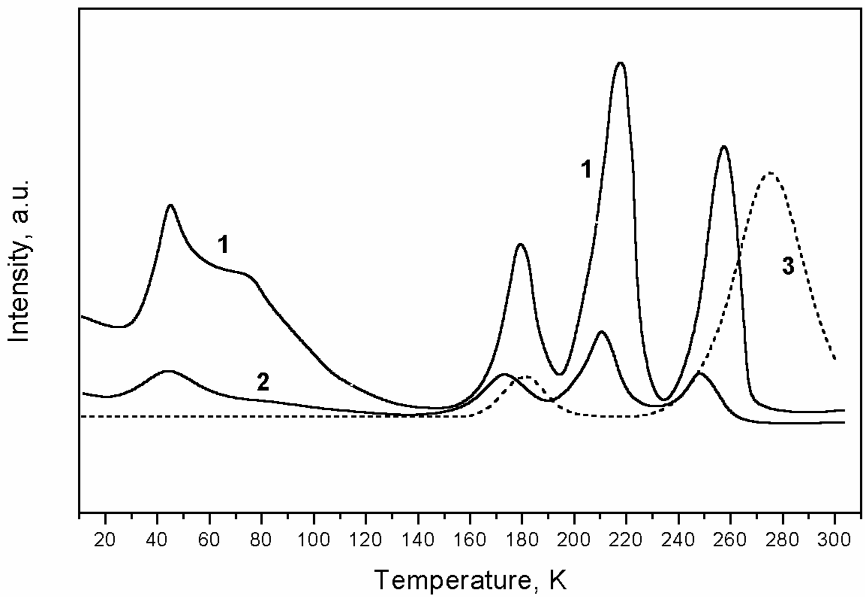

Fig. 5: The thermal glow curves of YAP-Tm (4 %) (1 – as-grown crystal; 2 – H_2-annealed) and YAP-Tm (1 %) as-grown (3).

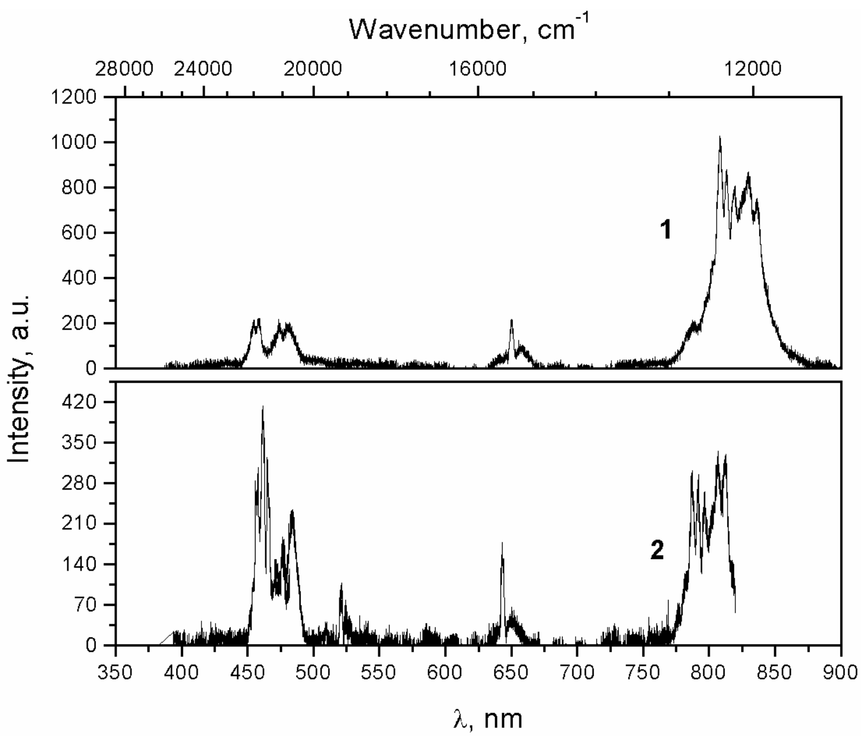

Fig. 6: The thermoluminescence spectra for YAP-Tm (1 %) at 280 K (1) and at 180 K (2).

The smaller intensity of defects luminescence in YAP-Tm (4%) in comparison with YAP-Tm (1%) crystal can be explained by greater concentration of Tm ions that can reabsorb the luminescence light (the intra-center transition $^3H_6 \rightarrow {}^1G_4$ of thulium lies in this region). It must be noted that due this reason we failed to record the excitation spectra of YAP-Tm (4%) crystal.

The presence of defect centers that can be trapping centers for charge carriers or recombination centers confirm also thermoluminescence studies of YAP-Tm. The thermal glow curves for investigated crystals are presented in Fig. 5. Two peaks of thermal glow at T~180 K and T~280 K were registered for YAP-Tm (1%) and four peaks at T~50 K, T~180 K, T~210 K and T~260 K were registered for YAP-Tm (4%) in 10–300 K temperature region. The thermal glow intensity decreases after the H_2 annealing of crystal. Spectra of thermoluminescence of YAP-Tm (1%) recorded at T~180 K and T~280 K are presented in Fig.6. As it is seen from the figure in both cases the thermoluminescence spectra coincide with photoluminescence spectra of thulium. The last observation testifies existence of interaction between Tm^{3+} ions and point defects. Energy becomes free at releasing of electron is transferred to thulium ions. At that the relative intensity of thulium peaks in thermoluminescence spectra is different at different temperatures. At T~280 K the luminescence in low-energy region dominates, and at T~180 K – in high-energy region (Fig.6). That testifies the different origin of defects destroyed at these temperatures. The energy transfer processes between color centers and activator ions were observed elsewhere in YAP-Er crystals (HUBER et al., 1998). To record the thermoluminescence spectra for YAP-Tm (4%) was not possible due to lower luminescence intensity.

4. Conclusions

It was shown that optical properties of both YAP-Tm (1 at.%) and YAP-Tm (4 at.%) crystals are determined mainly by presence of thulium ions. For as-grown YAP-Tm (4 at.%) crystals the absorption of defect centers was revealed to be essential. The presence of defect centers is apparent also in photoluminescence spectra of YAP-Tm crystals in the form of a wide band in blue-green region (25000-18000 cm^{-1}) that is excited in the band 25000-35000 cm^{-1}. Reducing annealing decreases concentration of growth defect centers and correspondingly improves optical properties of crystals. The main growth defects as in the case of other YAP crystals are antisite ions, oxygen vacancies, impurity ions and complexes of these defects. Thermoluminescence studies of YAP-Tm crystals confirm the possibility of energy transfer processes between defect centers and thulium.

Acknowledgements

The work was supported by the Ukrainian Ministry of Education and Science (projects No. 2M/50-2000 and 2M/49-2000).

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