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Spectral Properties of Oxide Crystals Free of Iron Ions

Al_2O_3 and YAG crystals were purified from traces of iron by the growth in reducing atmosphere. Luminescence output of such materials was substantially increased, but some undesirable properties as transient colour centre formation in YAG:Nd and low damage threshold of ruby laser rods were observed. Minimum concentration of iron ions which drastically change spectral properties of oxide crystals seems to be $\lessapprox 10^{-4}$ wt%.

Al_2O_3- and YAG-Einkristalle wurden durch Züchtung in reduzierender Atmosphäre von Eisenspuren gereinigt. Die Lumineszenzausbeute dieser Materialien wurde wesentlich erhöht. Es wurden jedoch einige unerwünschte Eigenschaften beobachtet, wie vorübergehende Farbzentren in YAG:Nd und ein niedriger Schwellenwert der Zerstörung der Rubinlaserstäbe. Es scheint, daß die minimale Konzentration an Eisenionen, die schon die spektralen Eigenschaften der Kristalle drastisch ändert, $\lessapprox 10^{-4}$ Gew.% beträgt.

1. Introduction

Thermoluminescence (TL) response of Al_2O_3 depends on several factors which complicate its preparation. The role of impurities (Cooke et al.) in minute concentration is practically unknown.

The emission from YAG:Ce^{3+} (e.g. under cathode-ray excitation) lying, on the contrary of other Ce^{3+} doped phosphors, in the visible region (Pawley) is also influenced by the presence of impurities. Earlier described YAG:Ce^{3+} showed luminescence efficiency and decay time to be dependent on thermal treatment.

Finally, a small concentration of impurities in laser ruby (Borer et al. 1970; Bashuk, Grum-Grzhimailo 1966) and YAG:Nd (Krupke) plays a special role owing to the extremely large excitation power used for the pumping of the active material in comparison with materials used as scintillators or dosimeters. The purpose of this paper is to summarize the properties of iron-free Al_2O_3 and YAG known up to date.

2. Experimental

Al_2O_3 and YAG crystals were grown by the Czochralski method using molybdenum or tungsten crucibles and 98% Ar(He)-2% H_2 protective atmosphere (Perner et al.). It enables after 40–50 hours of melting to remove the traces of iron ions which are always present in chemically purified raw materials. The crystals grown from such melts showed Fe contents below 1 ppm, i.e. less than sensitivity of the spectral or neutron activation analysis used (Kvapil et al. 1980 a). Nevertheless, the crystals or their parts grown immediately after melting of the raw material or those grown under atmosphere containing small amounts of hydrocarbons may be doped with Fe up to 10^{-2} wt%. (Kvapil et al. 1981 b.)

The charged electrodes above the melt level in the electrically conductive atmosphere and oppositely charged crucible enabled us to form an "oxidizing" or more reducing conditions in the neighbourhood of the melt/crystal interface which further influence the doping possibilities of the crystal.

Spectral and other measurements were accomplished by usual methods. Special methods are described in the following parts.

3. Results

a)Al_2O_3: Mo, Ti and Al_2O_3 :W, Ti crystals may be grown from the melt containing Ti ions using respective crucibles and positively charged (15 V) electrodes. The crystals free of iron ions show an extremely strong TL response (160 °C, 420 mm) which may be further increased by UV irradiation followed by thermal treatment at ~ 200 °C.

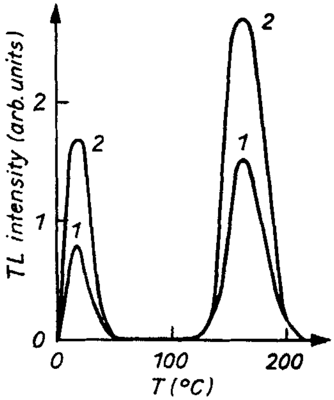

Fig. 1. TL spectra of γ-irradiated corundum crystals containing 2.10^{-3} wt% Ti and $3 \cdot 10^{-3}$ wt%Mo. 1 as grown, 2 irradiated by mercury lamp and annealed 10 min at 200 °C

The dose of γ-rays $\geq 10^{-7} - 10^{-6}$ Gy may be detected (Fig. 1). High temperature annealing($>$ 1500 °C) fully eliminates this luminescence. The same TL was observed on nominally undoped Al_2O_3 (Pujats et al.), Al_2O_3 :Mg, Y (Osvay, Biro), but the TL response seemed to be of less sensitivity and reproducibility than in the case of Al_2O_3 :Mo, Ti (Kvapil et al. 1980 b). TL and other properties of $Al:O_3$: W, Ti showed some difference from those of Al_2O_3 :Mo, Ti and they will be described in a separate article. TL of Al_2O_3 :Mo, Ti fully dissapears at Fe concentrations $\gtrsim$ 1—2 ppm.

b) Rubies showed TL with emission peaks at ~ 695 nm. TL temperature depends on the Cr content (Kvafil et al. 1980 b). The role of small amounts of iron ions ($\sim 5 \times 10^{-4}$ wt%) is rather questionable in this case because luminescence intensity and lifetime of Cr^{3+} decreases whereas TL response slightly increases, compared with iron-free ruby, particularly, when Mg^{2+} doped ($\leq 10^{-3}$ wt%) sample is used. The increase of Fe concentration in laser ruby from 1 to 10 ppm causes the laser output to be decreased 3.5 times, but damage threshold to be increased 7 times (Kvapil et al. 1981 b). Al_2O_3 and YAG doped with Fe showed absorption maximum peaked at 255 nm the absorption strength of which increases substantially in the presence of Cr ions (Kvapil et al. 1981 b). YAG :Nd free of iron ions showed the formation of transient colour centres (Fig. 2) with a lifetime of ~20 s at 20 °C. This absorption causes the mode degeneracy of YAG :Nd–CW laser and suppresses its output (Fig. 3) (Kvapil et al. 1981 a).

c) The experiments with cathode-ray excited YAG :Ce plates of 1 mm in thickness showed that the maximum luminescence efficiency had been achieved with samples

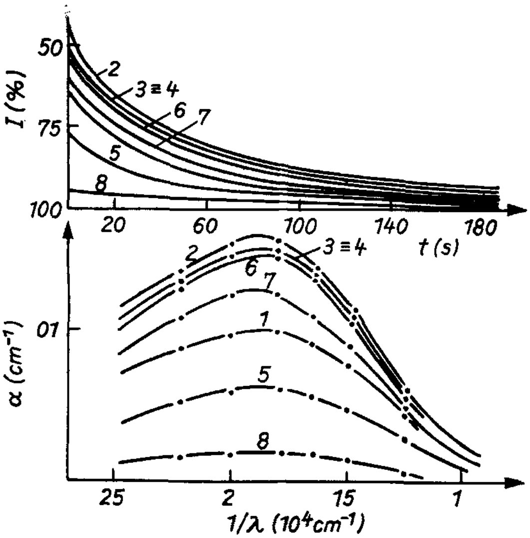

Fig. 2. The decrease of the absorption of the He–Ne laser light in the YAG :Nd rods (⌀ 6 × × 75 mm) after Xe lamp flashing (E_{in} = 600 J) (above) and transient absorption spectra of the same rods (below). 1 unannealed, annealed (1700 °C, 5 h); 2 in O_2; 3 in O_2 followed by H_2; 4 in vacuum, 5 in H_2; 6 in vacuum followed by H_2; 1 –6 and 8 –1 at. % Nd, 7 –0.7 at. % Nd; 8 filtered flashlamp light (absorption edge of the filter: 350 nm)

having the formula $Y_{2.985}Ce_{0.015}Al_5O_{12}$. A survey of the results obtained with the samples of this cerium concentration and some other phosphors used as scintilators for sequential electron microscopes is given in Figures 4 and 5 (Kvapil et al. 1980 c).

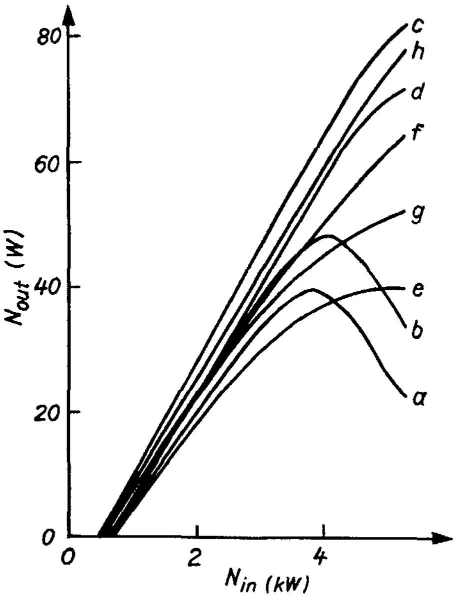

Fig. 3. CW output of the YAG rods ⌀ 6 × 75 mm. Absorption edge of the filter: a, b, c, d, e, f: 350 mm; g, h: 500 mm. R_{out} = 92 %, resonator length: 400 mm. Radius of the rear mirror: a, b, c, d, g, h: 5 m; e, f: ∞. Annealing: a, e, g: in O_2, followed by H_2, c, f, h – in H_2 d – in vacuum (crystal doped with $3 \cdot 10^{-4}$ wt % Fe)

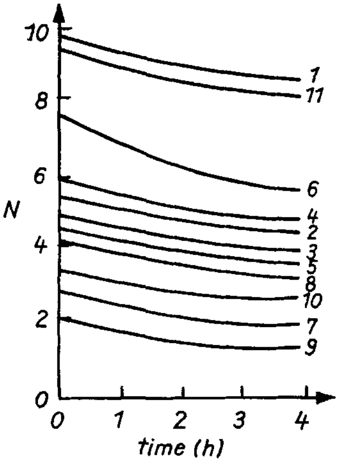

Fig. 4. The comparison of the luminescence output (N) – in arbitrary units – for different YAG :Ce^{3+} samples. Incident electron beam $E = 10$ keV, $J = 4 \cdot 10^{-8}$ A cm^{-2}; electron beam diameter 3 mm. 1 single crystal ($5 \cdot 10^{-4}$ wt% Mo) fired for 5 hours at 1500 °C in air and then powdered; 2 sample 1 fired for 50 hours at 1500 °C in air; 3 sample 2 fired for 5 hours at 1500 °C in H_2; 4 powdered single crystal (untreated) or the sintered cake melted in Mo crucible and powdered; 5 sample prepared by sintering at 1500 °C in air; 6 sample 5 fired for 5 hours in 98 % Ar + 2 % H_2, afterwards fired for 1 hour at 1400 °C in air; 7 sample 5 doped with 5 ppm Fe ions; 8 sample 5 doped with 5 ppm Ir ions; 9 sample 5 doped with 5 ppm Pt ions; 10 melted in Ir crucibles and powdered; 11 melted in Mo crucible, fired for 5 hours at 1500 °C in air and then powdered

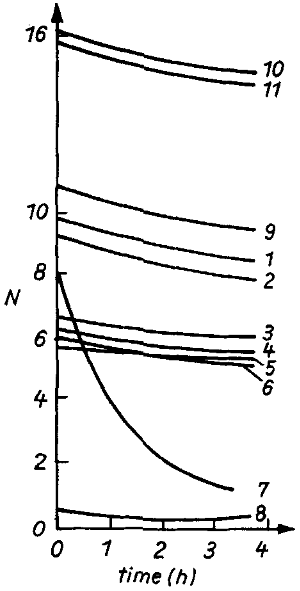

Fig. 5. The comparison of the luminescence output (N) – in arbitrary units – for different samples prepared from the YAG :Ce^{3+} single crystal with other Ce^{3+} activated phosphors. Experimental conditions see Figure 4. 1 single crystals fired for 5 hours at 1500 °C in air, afterwards powdered (see Fig. 4, sample 1); 2 single crystal ($5 \cdot 10^{-4}$ wt% Mo) plate fired for 5 hours at 1500 °C in air; one plane polished the matted one towards the photomultiplier, 3 plate as in 2. both planes polished; 4 $Y_2Si_2O_7$:Ce^{3+} powered sintered cake, 5 $Ca_2Al_2SiO_7$:Ce^{3+} powdered sintered cake; 6 scintilator for SEM JEOL; 7 plastic scintilator for SEM JEOL; 8 single crystal containing $2 \cdot 10^{-3}$ wt % Mo machined as sample 2; 9 as the sample 8 fired 5 hours at 1500 °C in wet hydrogen alumina crucible; 10 as the sample 9 but molybdenum crucible is used; 11 treated as the sample 10, but the crystal containing $5 \cdot 10^{-4}$wt % Mo is used

It is to be noted that decay time of YAG :Ce increases after hydrogen treatment (~ 150 ns) and decreases after an oxidizing one (~ 80 ns) or if it contained Fe ions.

4. Conclusions

VIIIb group ions possess numerous energy levels. Some of them may be in resonance with excited or thermodynamically stable states of the crystal matrix. Non-radiative energy transfer among energy levels of the VIIIb group ions is also possible. These phenomena cause that Fe admixture suppresses all the excited states of other dopants and unstable colour centres, whereas the formation of stable colour centres (e.g. in Al_2O_3 :Mg) is relatively easy. Besides of luminescence quenching Fe ions effectively suppress the population of the upper excited states of Cr^{3+} in Q-switched ruby where multiphoton absorption as a reason of crystal damage may be supposed.

5. Summary

Iron ions in Al_2O_3 and YAG crystals cause luminescence quenching of Ce, Cr, Ti, and Nd ions, suppress the formation of transient colour centres in YAG :Nd but increase the damage threshold of laser ruby. The phenomena described may be explained by the resonance between excited other dopants or colour centres and iron ions followed by non-radiative energy transfer among energy levels of iron ions.

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