Spectral Properties of Oxide Crystals Free of Iron Ions

Al₂O₃ 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 \(\lesssim 10^{-4}\) wt%.

1. Introduction

Thermoluminescence (TL) response of Al₂O₃ 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 :Ce³⁺ (e.g. under cathode-ray excitation) lying, on the contrary of other Ce³⁺ doped phosphors, in the visible region (Pawley) is also influenced by the presence of impurities. Earlier described YAG :Ce³⁺ 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 Al₂O₃ and YAG known up to date.

2. Experimental

Al₂O₃ and YAG crystals were grown by the Czochralski method using molybdenum or tungsten crucibles and 98% Ar(He)-2% H₂ 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) $\text{Al}_2\text{O}_3: \text{Mo, Ti}$ and $\text{Al}_2\text{O}_3: \text{W, Ti}$ 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 nm) which may be further increased by UV irradiation followed by thermal treatment at $\sim$ 200 °C.

![TL spectra of γ-irradiated corundum crystals containing 2.10⁻³ wt% Ti and 3·10⁻⁴ wt% Mo. 1 as grown, 2 irradiated by mercury lamp and annealed 10 min at 290 °C](image)

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 $\text{Al}_2\text{O}_3$ (PUJATS et al.), $\text{Al}_2\text{O}_3: \text{Mg, Y}$ (OSVAY, Biro), but the TL response seemed to be of less sensitivity and reproducibility than in the case of $\text{Al}_2\text{O}_3: \text{Mo, Ti}$ (KVAPIL et al. 1980 b). TL and other properties of $\text{Al}:\text{O}_3: \text{W, Ti}$ showed some difference from those of $\text{Al}_2\text{O}_3: \text{Mo, Ti}$ and they will be described in a separate article. TL of $\text{Al}_2\text{O}_3: \text{Mo, Ti}$ fully disappears at Fe concentrations $\leq 1 - 2$ ppm.

b) Rubies showed TL with emission peaks at $\sim 695$ nm. TL temperature depends on the Cr content (KVAPIL 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 Cr³⁺ decreases whereas TL response slightly increases, compared with iron-free ruby, particularly, when Mg²⁺ 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). $\text{Al}_2\text{O}_3$ 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 $\sim 20$ 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
Spectral Properties of Oxide Crystals Free of Iron Ions

Fig. 2. The decrease of the absorption of the He–Ne laser light in the YAG:Nd rods (6 x 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_{2.089}Ce_{0.015}Al_{0.1}O_{12}. A survey of the results obtained with the samples of this cerium concentration and some other phosphors used as scintillators 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 x 75 mm. Absorption edge of the filter: a, b, c, d, e, f: 350 mm; g, h: 500 mm. K_out = 92%, resonator length: 400 mm. Radius of the rear mirror: a, b, c, d, g, h: 5 m; e, f: ∞. Annealing: a, c, g: in O_2, followed by H_2, c, f, h: in H_2, d: in vacuum (crystal doped with 3-10^-4 wt.% Fe)
Fig. 4. The comparison of the luminescence output \( N \) — in arbitrary units — for different YAG:Ce** samples. Incident electron beam \( E = 10 \text{ keV}, J = 4 \cdot 10^{-5} \text{ A cm}^{-2} \); electron beam diameter 3 mm. 1 single crystal \((5 \cdot 10^{-4} \text{ wt} \% \text{ Mo})\) 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 \( \text{H}_2 \); 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 % \( \text{Ar} + 2 \% \text{H}_2 \), 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** single crystal with other Ce** 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 \((5 \cdot 10^{-4} \text{ wt}\% \text{ Mo})\) 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 \( \text{Y}_2\text{Si}_2\text{O}_5 : \text{Ce}^{3+}\) powered sintered cake; 5 \( \text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12} : \text{Ce}^{3+}\) powdered sintered cake; 6 scintillator for SEM JEOL; 7 plastic scintillator 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 Al₂O₃:Mg) is relatively easy. Besides of luminescence quenching Fe ions effectively suppress the population of the upper excited states of Cr³⁺ in Q-switched ruby where multiphoton absorption as a reason of crystal damage may be supposed.

5. Summary

Iron ions in Al₂O₃ 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.

References

Kvapil, J., Perner, B., Kubelka, J., Kvapil, J.,: Crystal Res. & Technol. 16, 1153 (1981) (b)
Osvay, M., Bíró, T.: Handling of Radiation Accidents, Vienna 1977, p. 493
Pawley, J. B.: Performance of SEM Symp. Chicago 1974, IITRI, p. 27

(Received December 14, 1981)

Authors' addresses:

J. Kvapil, B. Perner, J. Kvapil, B. Mánek, J. Kubelka, K. Blažek
Monokrystaly
Leninova 175
51119 Turnov, Czechoslovakia

R. Autrata, P. Schauer
Institute of Scientific Instruments, Czechoslovak Avademy of Sciences
Brno, Czechoslovakia

Z. Vitamvás
Technical University
Liberec, Czechoslovakia

59