Autolocalized excitons in Y_2O_3

A. I. Kuznetsov, V. N. Abramov, N. S. Rooze, and T. I. Savikhina

Physics Institute, Estonian Academy of Sciences
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Distinct luminescent manifestations of autolocalization of excitons in yttrium oxide have been observed.

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Up to now there was no known experimental proof of the existence of autolocalized excitons (ALE) in metal-oxide crystals. Nor was the existence of autolocalized holes (V_K) centers, which are typical of matrices with halogen anions and play a decisive role in the autolocalization of excitons in these matrices, been proved for oxides. The possibility of autolocalization of excitons was previously discussed for Al_2O_3,[1,2] for Y_2O_3, CaO and SrO,[2] for $Y_3Al_5O_{12}$,[3] and also for quartz SiO_2.[4]

A characteristic feature of the ionic crystal Y_2O_3(T_h^7, $\epsilon_\infty \approx 4$, $\epsilon_0 \approx 15$, $\Theta = 460$ K, $a = 10.6$ Å), which has prompted us to search for ALE, is the very complicated basis (16 formula units) and the fact that the neighboring sites of the crystal lattice are not identical[5]; this, in our opinion, should contribute to self-trapping of the quasiparticles. Excitons were previously observed in the absorption spectra of Y_2O_3 in Ref. 6. They have a small radius and a production energy 6.0 eV at a binding energy ~ 0.1 eV (see also curve 5 of Fig. 1). New data on the excitonic (zero-current) character of the 6.0-

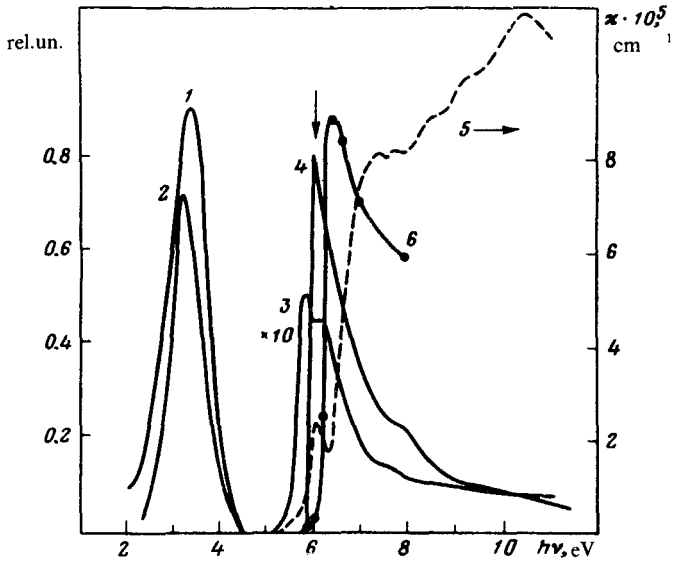

FIG. 1. Luminescence spectra of Y_2O_3 at 4.2 K (1, x-ray excitation) and 295 K (2, photoexcitation at $h\nu = 7.7$ eV); intrinsic-luminescence excitation spectra at 295 K (3) and 80 K (4); spectrum of fundamental absorption of Y_2O_3 at 295 K from the data of Ref. 6 (5); dependence of the light sum of the recombination radiation in Y_2O_3–Eu (5 mol. %) stored at 80 K on the energy of the exciting photons (6). The arrow indicates the position of the excitonic maximum (6.04 eV) at 80 K.

6.0-eV excitations in Y_2O_3 are seen on the spectrum 6 of Fig. 1. It determines the dependence of the light sum stored at 80 K (the area under the peaks of the thermal emission) of the recombination emission of europium in the Y_2O_3–Eu luminor on the energy of the exciting photons. It is seen that at 6.0 eV practically no light sum is stored, meaning in fact that the photocurrent due to irradiation in the (excitonic) absorption band at 6.0 eV is negligible at 80 K. The band structure of Y_2O_3 proposed in Ref. 6. is characterized also by a mixed *sd* character of the lower states in the conduction band.

The main purpose of the present study was a search for luminescence manifestations of autolocalization of excitons in Y_2O_3. We used the technique of vacuum ultraviolet spectroscopy, based on a Seya–Namioka type monochromator with hydrogen lamp as the source of the exciting light and with photoelectric registration of the luminescence spectra.[3] The luminescence spectra were registered with an MDR-2 or DMR-4 monochromator. For measurements at low temperatures we used nitrogen and helium cryostats. The quantum yield of the investigated luminescence was estimated by comparison with the luminescence of sodium salicylate. In some cases, x-ray excitation was used. The investigated objects were highly purified Y_2O_3 (99.99999%) powders roasted at 1300 °C, single crystals grown by the Verneuil method, and also the luminors Y_2O_3–Eu and Y_2O_3–Tb.

It was deduced from a large number of measurements that Y_2O_3 is characterized by a structureless luminescence band with a maximum of 3.45 eV at 4.2 K (3.3 eV at

295 K), a half width from 0.8 (4.2 K) to 1.0 eV (295 K), and a quantum yield at $T < 200$ K, $\eta \gtrsim 0.5$ (Fig. 1, curves 1 and 2). In the 4.2–160 K range, the emission intensity is practically constant (this was verified for x-ray and photoexcitation at $h\nu = 6.0$ eV), while at $T > 160$ K temperature quenching sets in, with an activation energy 0.275 eV, so that at 295 K the luminescence is weakened by a factor of 13 (Fig. 2, curve 1). The line-spectrum edge luminescence of free excitons could not be registered in the region 6.0 eV. The 3.4 eV emission is excited most intensively in the exciton absorption band of Y_2O_3 at 6.0 eV (Fig. 1, curves 3 and 4). Since no selective excitation bands are observed for this emission in the transparency region of Y_2O_3, it was suggested that this emission belongs not to impurities or defects, but to ALE. The parameters of this luminescence are large, with the quantum yield ($\eta \gtrsim 0.5$), the Stokes shift (2.6 eV), and the band width typical of ALE.

The fact that the ALE luminescence intensity is independent of temperature in the region 4.2–160 K distinguishes Y_2O_3 from alkali-halide crystals and from inert-gas crystals, in which the luminescence yield of the (two-site) ALE decreases at very low temperatures because the excitons overcome the energy barrier on going to the autolocalized state.[2,7,8] Curve 1 of Fig. 2 indicates that in Y_2O_3 the autolocalization takes

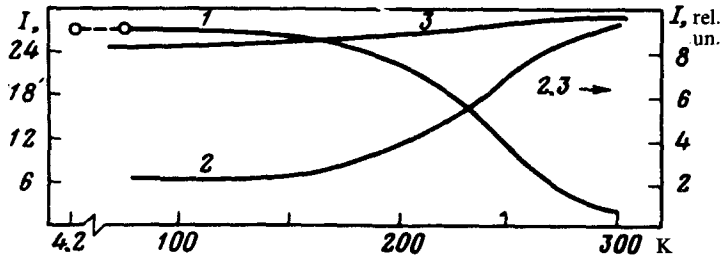

FIG. 2. Temperature dependence of the intensity of the emission in "pure" Y_2O_3 and in the luminor Y_2O_3–Tb (0.25 mol. %): for the 3.4-eV band (1) and for the Tb activator (2,3) with excitation at $h\nu = 6.0$ (1,2) and 8.0 eV (3). The points on curve 1 mark the normalized intensity of the x-ray luminescence.

place with practically no barrier, i.e., very rapidly. Since the ALE mobility is usually very small, the excitons should not take part in energy-transfer processes in Y_2O_3 at a temperature $T < 160$ K.

In fact, it was observed that at temperatures 4.2–160 K, when the excitons are optically produced by photons of $h\nu = 6.0$ eV, the 3.4-eV emission band is the only one present since the various emission bands observed at 295 K are of impurity–defect origin and vanish at the low temperatures. The effect is particularly pronounced for the luminor Y_2O_3–Tb (0.25 mol. %) (Fig. 2, curve 2). It is important that the decrease of the intensity of the characteristic emission of the terbium ions (filters were used to separate the lines at 550 nm) takes place in the course of cooling simultaneously with the increase of the intensity of the 3.4-eV ALE emission (curve 1), thus attesting to a connection between these phenomena. The "residual" luminescence of Tb at $T < 140$ K is apparently due to reabsorption, since the short-wave edge of the 3.4 eV band overlaps with the activator excitation band of Tb.[9] We note that the fact that the light

sum of the recombination radiation is not stored when excitons are produced in the Y_2O_3–Eu luminor (spectrum 6, Fig. 1) also means that the excitons do not transfer energy to different trapping centers.

Nor do the excitons in Y_2O_3 transfer energy to the surface at low temperatures. This explains the substantial difference between the excitation spectra of the 3.4-eV emission measured at 295 and 80 K (Fig. 1, curves 3 and 4). At 295 K, a dip typical of the case of mobile excitations is observed in the exciton maximum of the absorption at 6.0 eV, since an increase of the absorption coefficient causes excitation of a thin surface layer, and the nonradiative losses on the surface are large because of migration of the exciting energy on the surface. At 80 K there is no selected excitonic dip in the excitation spectrum (despite the somewhat greater selectivity of the excitonic absorption at 80 K, Ref. 6), and this should be typical of low-mobility excitations. At 295 K, the dip at 6.0 eV can be due to thermal activation diffusion of ALE and (or) dissociation of the excitons into mobile electrons and holes. Curve 3 on Fig. 2 demonstrates that in the case of (interband) excitation of free electrons and holes there is practically no freezing of the activator luminescence in Y_2O_3–Tb. This may mean that the mobility of the carriers does not change significantly in the region 295–80 K. This seems to be an important fact and must be taken into account in future studies of the mechanism of autolocalization of excitons in Y_2O_3.

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