Exciton creation in LuAlO₃ single crystalline film

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Single crystalline films (SCF) of LuAP attract attention because of the perspective of its application as 2D screens for X-ray registration with high spatial resolution. An intensive sharp reflectivity peak at the edge of the fundamental absorption region with maximum at 8.37 eV at 10 K was found for a series of LuAP SCF grown by liquid phase epitaxy on YAP substrate. The dependence of the peak maximum and profile on temperature demonstrates its exciton origin. The absorption spectrum was calculated from reflectivity using Kramers–Kronig relations; the bandgap value was determined for LuAP as E_g = 8.44 eV at 10 K.

1 Introduction The LuAlO₃ (LuAP) single crystals (SC) doped with Ce³⁺ attract attention as fast scintillators for positron emission tomography and an intensive study of this crystal was performed recently [1]. Also LuAP:Ce single crystalline films (SCF) grown by liquid phase epitaxy (LPE) were investigated as the material for 2D screens for X-ray registration with high spatial resolution [2]. SCF is an attractive object for investigation because of the lower concentration of structure defects when compared with bulk crystals [3].

In spite of the LuAP application perspective its energy band structure is almost unexplored. In particular the question concerning the possibility of exciton creation at the edge of the fundamental absorption region (FAR) is still open. Actually the existence of the exciton frequently determines the character of the energy transfer to emission centers. To our knowledge there is no information about theoretical calculations of the LuAP density of states. However, on the basis of the photoemission spectrum [4], it was assumed that the top of the valence band is composed of O 2p states. The position of the first reflectivity peak in LuAP is mentioned to be at 8.5 eV in [5]. Reflectivity of the LuAP SC crystal in FAR was analyzed in [4]. A low-intensity shoulder was observed at the edge of FAR

in LuAlO₃ as well as in the isostructural YAlO₃ [6, 7] and it is connected with exciton creation. Nevertheless this assumption requires correct approvement.

In this paper we report on the reflectivity of a series of LuAP SCF. Evidence of exciton creation at the edge of FAR is presented. Data obtained from the Ce³⁺ luminescence excitation spectra confirm the exciton existence.

2 Experimental details The measurements of reflectivity and luminescence excitation spectra were performed at the Superlumi station (DESY, Hamburg, Germany) [8] in the energy region of 7–22 eV at temperatures from 10 to 300 K. The angle between surface normal and incident synchrotron radiation was 17.5°. The obtained spectra were normalized to the quantum efficiency of sodium salicylate. Luminescence excitation spectra were measured synchronously with reflectivity that allow to compare these results correctly in the forthcoming discussion. Four samples of LuAP SCF grown by LPE on YAP substrate using liquid phase epitaxy were investigated. Three of them were undoped samples with SCF thickness of 5.4, 22 and 23 μm. The investigated LuAP:Ce SCF was grown on (100) oriented YAP substrate at T = 972–969 °C. The CeO₂ con-

centration in the melt was 13 mol%. The thickness of the LuAP:Ce SCF was about 3 µm.

Calculations of the absorption spectrum from reflectivity were performed using Kramers–Kronig relations. The refractive index in the transparency region was used as reference parameter. The reflectivity above 22 eV was approximated by the $(h\nu)^{-4}$ law. A more detailed description can be found elsewhere [9].

3 Results and discussion Reflectivity was measured for all four investigated samples. The reflectivity peak in the energy region of exciton creation was observed for all samples, though its sharpness is sample dependent. The sharpest peak was observed in the reflectivity of the LuAP:Ce SCF sample with thickness of 3 µm and in the undoped LuAP SCF with thickness of 23 µm. In the two other samples this peak is less pronounced and broadened. We suggest that its sharpness is connected with the quality of the LuAP SCF single crystal structure in the thin surface layer. Actually when the absorption coefficient has the order of magnitude 10^5–10^6 cm^{-1} the absorption of the incident radiation is realized in the layer with thickness of 0.1 µm.

Figure 1 presents the LuAP:Ce reflectivity at $T = 10$ K. A pronounced reflectivity peak with maximum at 8.37 eV is observed at the edge of the fundamental absorption region (FAR). In the inset the temperature dependence of this reflectivity peak position and shape is presented. It can be seen that with temperature increase the peak shifts to the low energy region and broadens. The value of the peak maximum at corresponding temperature is presented in Table 1. Such behavior is typical of excitons at the edge of FAR. The temperature dependence of the exciton peak maximum and its profile is due to the exciton–phonon interaction [10].

This exciton peak was not observed for LuAP [4] or for isostructural YAP [6, 7] single crystals before. The

Table 1 Energy position of the exciton peak as function of the temperature in reflectivity of LuAP SCF.

T (K)	E_{max} (eV)
10	8.37
50	8.37
100	8.36
150	8.33
200	8.30
250	8.26
300	8.24

shoulder in the absorption spectra calculated from reflectivity using Kramers–Kronig relations in the region of 8.1–8.3 eV was observed in [4, 7] and its temperature dependence was not determined. It was also treated as exciton and the low intensity of the exciton was connected with the low probability of its creation in favor of the electron–hole pair creation in LuAP [4]. However, our results allow to suggest, that the imperfection of the crystal structure and defect presence in the bulk crystal is the main reason why it was not observed before for bulk samples. We assume that the presence of a distinct exciton peak can be used as indicator of the single crystal structure perfection and of the absence of a reasonable concentration of defects in SCF.

The LuAP absorption calculated using Kramers–Kronig relations from experimental reflectivity measured at 10 K is presented in Fig. 2. The absorption allows to obtain more precise energy values of electron transitions. Thus the energy of the exciton creation at 10 K is 8.38 eV. The energy position of the other absorption peaks in the energy region of 8.5–22 eV is presented in Table 2. The bandgap value for LuAlO$_3$ determined by the beginning of rise of the absorption coefficient on the high-energy edge
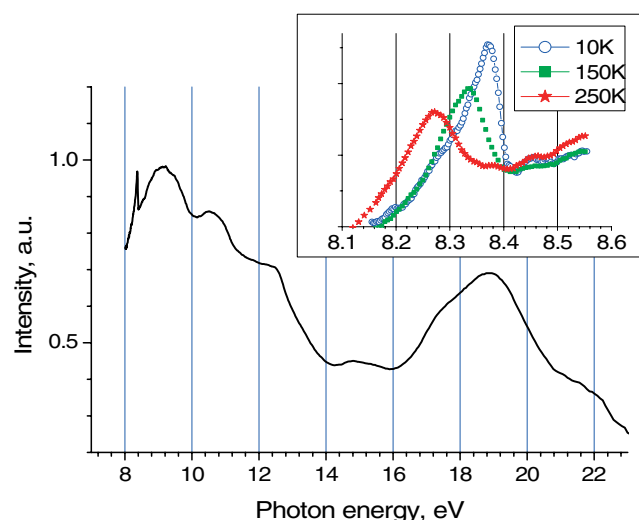

Figure 1 (online colour at: www.pss-rapid.com) Reflectivity spectrum of LuAP:Ce at 10 K. In the inset: Temperature dependence of the energy position of the exciton peak in LuAP.
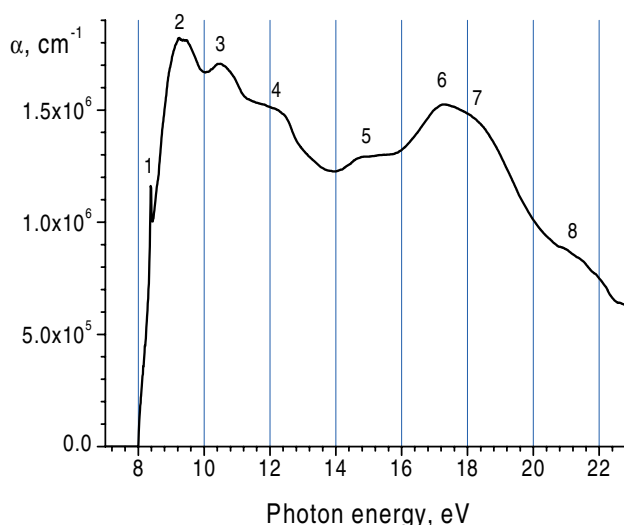

Figure 2 (online colour at: www.pss-rapid.com) Absorption spectrum of LuAP, calculated using Kramers–Kronig relations from reflectivity, 10 K.

Table 2 Energy position (in eV) of the absorption peaks from Fig. 2 in LuAP at 10 K.

1	2	3	4	5	6	7	8
8.38	9.3	10.5	12.2	15.0	17.3	18.2	21.0

of the exciton peak can be estimated as $E_g = 8.44$ eV at 10 K.

Absorption and Ce3+ luminescence excitation spectra of fast (measured in time intervals of 5–40 ns after the excitation bunch) and slow (115–170 ns) components measured at 100 K are presented in Fig. 3. In the fast component of luminescence excitation a sharp rise starting at 8.2 eV is observed. It is connected with the beginning of photon absorption on LuAP at the low-energy side of the exciton absorption. The maximum of exciton absorption coincides with the maximum in the fast component of the excitation spectra. In this energy region the excitation of cerium emission is realized via exciton migration to the emission center. At higher energies just above the exciton maximum besides the fast component a rise in the slow component of excitation spectrum is observed. This component is due to the excitation of cerium center via separated electrons and holes that can be trapped. Thus the slow component shows the FAR edge with the creation of separated electrons and holes and verifies the conclusion about the exciton character of the first absorption peak and about the bandgap value.

4 Conclusion The reflectivity and luminescence excitation spectra of a series of LuAP SCF were measured. Exciton creation at the edge of the fundamental absorption region was proved by the temperature dependence of the exciton peak. The exciton reflectivity peak maximum shifts with temperature from 8.37 eV at 10 K to 8.24 eV at 300 K. The bandgap value was determined by the beginning of rise of the absorption coefficient on the exciton high-energy edge and was estimated as $E_g = 8.44$ eV at 10 K.

Figure 3 (online colour at: www.pss-rapid.com) Absorption (black line) together with fast (5–40 ns, red, circles) and slow (115–170 ns, green, squares) components of the Ce^{3+} luminescence excitation spectrum ($\lambda_{em} = 380$ nm), $T = 100$ K.

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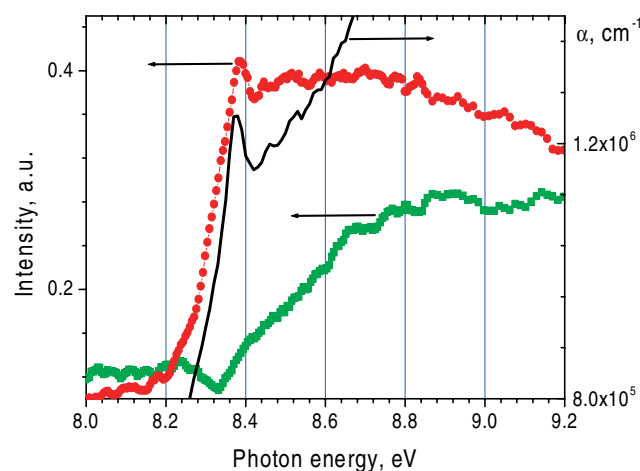[10] R. S. Knox, Theory of Excitons (Academic Press, New York, 1963).