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YEREVAN PHYSICS INSTITUTE

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VACUUM ULTRA-VIOLET LUMINESCENCE EXCITATION SPECTRA OF α-Al_2O_3 SINGLE CRYSTALS

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α-Al_2O_3 ԲՅՈՒՐԵՂՆԵՐԻ ԼՅՈՒՄԻՆԵՍՑԵՆՑԻԱՑԻ ԳՐԳՈՒՄԱՆ ՎՈՒՄ ԵՐԱՆԳԱՆԻՆԵՐԸ

Օգտագործելով բարձր ատիճանի բևեռացված սինքրոտրոնային ճառագայթումը հետազոտված է 5-35 էվ տիրույթում լյումինեսցենցիայի գրգռման սպեկտրները: «Մաքուր» շափյուղի միաբյուրեղների, որոնք աճեցված են հորիզոնական աճեցման մեթոդով՝ ճառագայթված 50 ՄէՎ էլեկտրոններով: Սինքրոտրոնային գրգռումը թույլ է տվել հայտնաբերել սեփական կլանման եզրից ցածր 3,8 շերտի լյումինեսցենցիայի 6,3; 7 և 8 էվ գրգռման շերտերը, որոնք համընկնում են F^+- կենտրոնի կլանման շերտերի հետ, ինչպես նաև Cr^{3+}- իոնի R-գծերը: Վերջինս բացատրում է էքսիտոնի լիցքերի փոխանցումը Cr^{2+} և Cr^{4+}- իոններին: $h\nu>9,5$ էվ էներգիայից բարձր տիրույթում նկատվել է անկում, որը բացատրվում է ներատոմակերևութային շերտերի ոչ ճառագայթային ռեկոմբինացիաներով, որոնց հավանականությունը ուժեղ կլանումների դեպքում կտրուկ մեծանում է: Ճառագայթումից հետո տեղի է ունենում շափյուղի բյուրեղների լյումինեսցենցիայի շերտերի շեղում և ելքի փոփոխություն: Լյումինեսցենցիայի արդյունավետության աճը կապված է ինչպես ճառագայթման, այնպես էլ չճառագայթված շափյուղի բյուրեղների էլեկտրոնային գրգռման բավմապատկմամբ:

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V.V.HARUTUNYAN, V.A.GEVORKYAN, N.E.GRIGORYAN

VACUUM ULTRA-VIOLET LUMINESCENCE EXCITATION SPECTRA OF α-Al_2O_3 SINGLE CRYSTALS

The luminescence excitation spectra of corundum single crystals irradiated with 50 MeV electrons were studied. In the region of fundamental absorption there appeared excitation bands (blue and ultra-violet) which correlated well with optical absorption bands of the F^+-centre in the absorption (reflection) spectra. The excitonic peaks observed in the excitation spectra of red luminescence were explained by the charge energy transfer by Cr^{2+}, Cr^{4+} ions at excitonic excitation At $\hbar\nu > 9.5$ eV there appeared sharp drops which were interpreted as nonirradiative near-surface recombinations, whose probability sharply increased at high absorption coefficients. The enhancement of the luminescence efficiency in the high-energy region was connected with the decay effect of electron excitations as well as with the influence of volumetric excitations leading to the enhancement of recombination glow.

Yerevan Physics Institute

Yerevan 1990

Препринт ЕФИ-1278(64)-90

В.В.АРУТЮНЯН, В.А.ГЕВОРКЯН, Н.Е.ГРИГОРЯН

ВУФ СПЕКТРЫ ВОЗБУЖДЕНИЯ ЛЮМИНЕСЦЕНЦИИ КРИСТАЛЛОВ α-Al_2O_3

С использованием высокой степени поляризации СИ исследованы спектры возбуждения люминесценции в области 5-35 эВ номинально "чистого" монокристалла корунда, выращенного методом горизонтальной направленной кристаллизации и облученного 50МэВ-ными электронами. СИ возбуждение позволило обнаружить в области ниже края собственного поглощения 6.3; 7; 8 эВ люминесценции 3,8 эВ, совпадающие с полосой поглощения F^+-центра, а также полосы R-линии неконтролируемой примеси Cr^{3+}. Последняя объясняется переносом энергии экситонного возбуждения на ионах $C_2^{2+}Cr^{4+}$. При энергии $h\nu > 9,5$ эВ наблюдаются провалы, которые являются следствием безызлучательных приповерхностных рекомбинаций, вероятность которых резко возрастает при больших коэффициентах поглощения. После радиационного воздействия происходит смещение и изменение выхода свечения. Возрастание эффективности свечения связано с эффектом [illegible] электронных возбуждений как в облученных [illegible] в необлученных кристаллах корунда.

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Of particular interest is the study of optical properties (colour centres) of corundum which are absorbed in the ultra-violet (UV) and vacuum ultra-violet (VUV) regions and irradiate UV spectra, with the aim to construct lasers generating in this range of spectrum.

Earlier in the absorption spectra of electron-irradiated [1,2] and neutron-irradiated [3] corundum we had revealed experimentally the optical absorption (OA) bands: 4.86,5.4, 6.3, 7 and 8 eV which attributed to the F^+-centre.

The goal of the present work is to obtain additional information to confirm the identification of the earlier found OA bands over luminescence excitation spectra (LES) of corundum single crystals.

In the energy range from 5 to 30 eV there were measured the luminescence excitation (LE) spectra on a"Sibir-1" VUV light source [4].

The corundum single crystals, 10x15x1.7mm, grown by the method of horizontal-oriented crystallization were used.

The optical axis C_3 was parallel to the larger edge of the samples.

The samples were irradiated with 50 MeV electrons at the

inac of the Yerevan Physics Institute. They were cooled by iquid nitrogen vapour. Irradiation dose was $6 \cdot 10^{17}$ e cm^{-2}. Spectra were taken off at 295 k. The samples luminescence was detected with a PEM-100 in the regime of single photon counting.

Note that the LE spectra detection was done in SR orientation $\vec{E} \perp C_3$, since in this case all OA bands are pronounced.

Fig.1 shows the OA spectra of the nonirradiated single crystal (curves 1,2) and of those irradiated with the electrons (curve 3) and reactor neutrons with a dose of 10^{17} n cm^2 (curve 4). From Fig.1 (curves 1,2) one can see the OA bands:4.86, 5.4, 6.2-6.4 and 7-7.3 eV. After irradiation the bands 4.86, 6.1, 6.3 and 7 eV can be found in the absorption spectra (curve 3). In the neutron irradiation case there appears, in addition, a band in the region 7.9 eV (curve 4) which is predicted theoretically in Ref. [5}. The band of 7.9 eV after electron irradiation irregularly appears in the absorption spectra because of the comparability of the spectrum measurement error with a sharp increase in the absorption coefficient. The concentration of colour centres at neutron irradiation in considerably higher, owing to which the given band is clearly pronounced in the OA.

The investigations have shown that in the fundamental absorption region in the LE spectra one can see clearly pronounced relatively narrow bands of irradiated and nonirradiated corundum crystals. Some bands in the LE spectra up to the edge of fundamental absorption within the experimental error ± 0.1 eV correlate well with the absorption

spectrum. Hence, in the LE spectra part of bands are due to intracentre transitions. Besides, a nonirradiative process without/with charge transfer is possible.

It is known that the OA bands of the $F^{\pm}$-centre at high-energy quanta excitation give a luminescence of 3.8 eV (UV), and the F-centre (6.1 eV)-3.0 eV (blue) [6].

Figs.2 and 3 present the LE bands, the intensity of irradiated samples being considerable higher: 5.35, 5.5, 5.9, 6.3 and 7.9 eV. The number of LE bands exceeds that of OA bands (FIg.1) because the LES are more sensitive to the excitation energy than the absorption spectra are. The appearance of such a number of glow bands may be due to the fact that in the LE spectrum there is available the luminescence of F- and F^{+}-centres as well as the luminescence of uncontrollable impurities of chromium and other ions of the iron group, and finally, the luminescence of self-localized and localized excitons near their own defects and impurity ions.

Indeed, the existence of excitons is confirmed by the presence of bands in the reflection spectra and LES; the bands are slightly shifted in the region 8.9-9.2 eV because of the change in the magnitude of electrostatic field $\vec{E}$ at irradiation, which affects the set of both defects and excitons.

The band of 5.35 eV in the LES belongs to the F^{+}-centre, is excited in its own absorption band of 5.4 eV and produces a weak blue glow. In the UV glow band (Fig.3) the intensities of 5.35 eV bands of irradiated and nonirradiated crystals almost coincide. The 5.55 eV band, presumably, is also due to the F^{+}-centre and was predicted in [8] (5.7 eV).

In the spectra of the blue and UV glow there is pronounced a band of 5.9 ± 0.1 eV which coincides with the absorption band of the F-centre. The excitation band of 6.3 ev is clearly pronounced in blue glow and is attributed to the F^+-centre of absorption [2], but may be insignificant in the UV glow because of the sharp increase of the latter.

Of particular interest is the LE band of 8.2 ± 0.1 eV which is somewhat shifted as compared to the OA band and has a large intensity in the irradiated crystals in the blue glow case. In the LE spectra one can observe also weak exciton excitation in the region of 9 eV which are intensely pronounced in the red glow of the Cr^{3+} R-line [7]. Such a behavior of the exciton excitation bands can be explained by the electron excitation (EE) energy transfer by means of charge tunneling on Cr^{4+} and Cr^{2+} ions with the subsequent formation $(Cr^{3+})^* \rightarrow Cr^{3+} + \hbar\nu_R$.

Comparing results on the study of the LE spectrum up to the fundamental absorption edge with the reflection (absorption) spectra, one can conclude that there occurs intracentre excitation of luminescence by own defects and uncontrollable impurity ions, a nonirradiative EE energy transfer, EE energy transfer by excitons and EE energy transmission with charge transfer.

In the energy range 9.55-22 eV in the LES one can observe a decrease in luminescence efficiency for irradiated and nonirradiated single crystals and antisymbateness to the reflection spectrum is pronounced. The same picture is observed also for some other wide-zone single crystals [8].

As a reason for such a behavior of LE spectra one should regard nonirradiative near-surface charge recombination whose

probability sharply increases at high absorption coefficients and small depth of light penetration into the crystal.

Besides, the may be different elementary excitation of glow centres as well as plasma excitations.

The threshold of electron excitatien multiplication begins at $\hbar\nu > 22$ eV, which makes up $>2E_g$ in this case the efficiency of the blue and UV glow increases due to the fact the fast photoelectrons scatter on the valence electrons and generate slow secondary electron-hole pairs. The recombination of the secondary-hole pairs by pre-irradiation defects of a single crystal gives rise to a wide-band glow which embraces the region of the blue and UV glow, this being just the reason for the identity of excitation bands in the LE spectra.

Besides, the exciting photon energy penetrates deep into the crystal because of the decrease of reflection and increase of participation of volumetric excitations, which just leads to a considerable increase of the number of electron-hole pairs which in turn enhance the recombination glow efficiency.

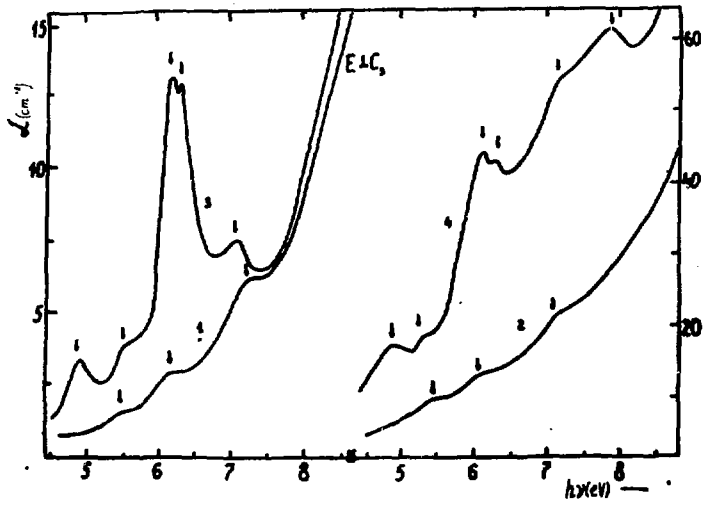

Fig.

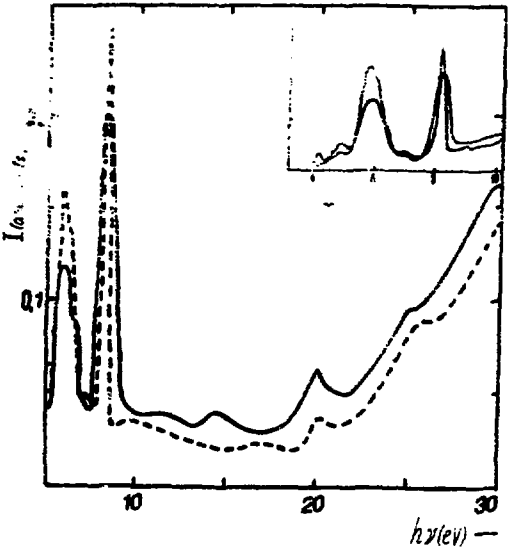

Fig.2

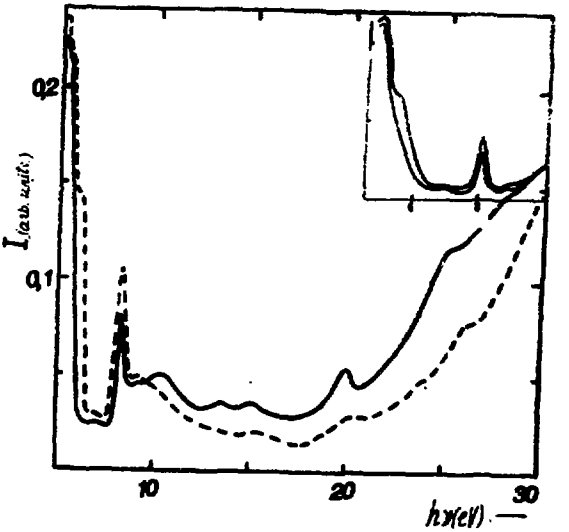

Fig.3

Figure Captions

Fig.1. OA spectra of corundum: 1,2 - nonirradiated crystal; 3-irradiated with a dose of 6 x 10^{17} e/cm^2; 4-irradiated with a dose of ~10^{17} n/cm^2.

Fig.2. Luminescence excitation spectra (filter SS-5, 420mm). Solid curve - nonirradiated crystal; dotted curve - irradiated with a dose of 6 x 10^{17} e/cm^2.

Fig.3 Luminescence excitation spectra (filter UFS-2,315 NM). Solid curve - nonirradiated crystal; dotted curve - irradiated with a dose of 6 x 10^{17} e/cm^2.

References

1. Harutunyan V.V., Grigoryan N.E., Gevorkyan V.A., Eritsyan H.N. Nuclear Instruments and Methods in Physics Research. 1989, vol.282, p.622.
2. Harutunyan V.V., Gevorkyan V.A., Grogoryan N.E., Eritsyan H.N., Martirossyan U.M. Fizika Tverdego Tela, 1988, vol.30, p.2307.
3. Harutunyan V.V., Gevorkyan V.A., Grigoryan N.E., Eritsyan H.N. Preprint YERPHI-1200(77)-89, Yereva, 989.
4. Ternov I.M., Mikhailin V.V. Synchrotron Radiation. Theory and Experiment, Moscow, "Energoatomizdat", 1986, p.295.
5. Choi S.J., Takeuchi T. Phys.Rev.Lett. 1983, vol.50, p.1474.
6. Lee K.H., Crawford J.H. Jr. Phys.Rev., 1977, vol.B15, p.4065.
7. Harutunyan V.V., Gevorkyan V.A., Grigoryan N.E., Eritsyan H.N. Preprint YERPHI-1183(60)-89, Yerevan, 1989.
8. Vasil'ev A.N., Kolobanov V.N., Kuusman I.L., Luschik G.B., Mikhailin V.V., Fizika Tverdogo Tela, 1985, vol.27, p.2697.

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ВУФ СПЕКТРЫ ВОЗБУЖДЕНИЯ ЛЮМИНЕСЦЕНЦИИ

КРИСТАЛЛОВ α-Al_2O_3

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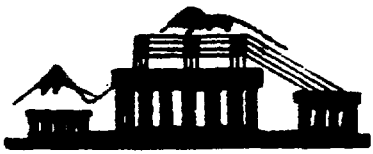

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