METHODS OF RESEARCH OF MINERALS, ROCKS, AND ORES

Synchrotron-Excited Luminescence of Natural Zircon

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Abstract—The luminescence properties of two single zircon crystals from kimberlite of Yakutia have been studied, excited by the DORIS HASYLAB synchrotron, Germany, within energy range from the visible to the soft X-ray region (5−25, 50−200, and 500−620 eV) at temperatures of 300 and 10 K. The luminescence spectra in the range of 2.5 to 6.0 eV and excitation spectra of the main bands have been examined, the physical nature of the luminescence centers has been discussed, and the luminescence properties of a crystal containing growth (radiation) structural defects and a crystal with the same impurities but annealed in air at 1200°C are compared. The zoned structure of the mineral has been considered and the value of the energy gap (E_g) in the mineral has been estimated at 7.1 eV. Two groups of luminescence bands caused by impurities of intrinsic (growth, radiation) nature ($E_{max} = 2.1, 2.7−2.8,$ and $3.2−3.3$ eV) and matrix luminescence ($E_{max} = 4.4−4.7$ and 5.4 eV) probably with the participation of excitons were distinguished on the basis of selective excitation of zircon with different synchrotron energies relative to the gap value ($E_{excit} < E_g$, $E_{excit} \sim E_g$, and $E_{excit} \gg E_g$). The short-lived component with a response time of 4 ns has been revealed in the afterglow of zircon in the region of 5.4 eV.

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INTRODUCTION

The long research history of luminescence of inorganic natural and synthetic compounds (minerals, ceramics, and glasses), which started from descriptive investigations in the early 20th century with only visual documentation of glow, has continued in the late 20th century, when the spectra and kinetics of photo-, X-ray-, thermal-, and cathode-induced glow were examined and the nature of impurity and proper luminescence centers (LC) for the overwhelming majority of minerals and their synthetic analogues was interpreted. Currently, luminescence studies are focused on the glow induced by synchrotron radiation (SR); numerous synthetic crystals, in particular, various oxides with a complex sublattice, are studied; in contrast, there are no publications on natural compounds.

What has caused the heightened interest in luminescence experiments with SR, which require large capital investment to create scientific joint centers? The use of SR to excite glow in solids provides insights into their electron structure, including the nature of intrinsic luminescence and structure of defects, and the formation, effects of autolocalization, and radiative decay of excitons, which are linked electron−hole states.

In a synchrotron, accelerated electrons generate high-power electromagnetic radiation in a wide range of energy from fractions and a few eV (IR, visible, UV,

and VUV regions) to hundreds of keV (X-ray region) with a continuous spectrum, high degree of polarization, large intensity (several orders higher than X-ray tubes), extremely small divergence, and short pulse duration (down to 10^{-10} s). Currently, about 50 synchrotrons of various generations characterized by different power and SR quality operate in 18 countries. The European Synchrotron Radiation Facility, Grenoble, France; Spring-8, Japan; Advanced Photon Source, Aragon National Laboratory, United States; and DORIS, HASYLAB, Hamburg, Germany, are third-generation.

Natural zircon is a brightly luminescent mineral; luminescence methods are widely involved in studying its impurity and intrinsic defects. Such investigations are of great importance, in particular, to resolve the problem of closure of the U,Th−Pb isotope system in determining the isotopic age of zircons and predicting the retention of zircon ceramics, which is promising for utilizing radioactive elements, for example, weapons-grade plutonium (Ewing et al., 2003). Luminescence of zircon is rather effective in petrology: genesis of the mineral, its thermal stability, and radiation history affect its glow. Numerous studies are concerned with zircon luminescence induced by different types of excitation: cathode (Hanchar, Rudnic, 1995; Gotze et al., 1999; Kempe et al., 2000; Remond et al., 2000; Poller et al., 2001), photo (Tarashchan, 1978; Votyakov et al., 1986), X-ray (Krasnobaev et al., 1988), laser (Gaft et al., 2002), ionic (Correcher et al., 2007), and thermal (Kirsh, Townsend, 1987; Krasnobaev et al.,

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Energy (E) and half-width (ΔE) of the strongest SEL bands in zircon I and II at 300 and 10 K

Sample of zircon	T, K	E and ΔE, eV					
		D(Fe^{3+})?	C	B1	B	A_2	A_1
I	300	1.76	2.12	2.60	3.38	–	4.95
		0.2	0.36	0.31	0.98		0.89
	10	–	2.22	2.69	3.31	4.38	4.81
			0.42	0.32	0.82	0.57	0.82
II	300	1.83	2.20	2.70	3.45	–	4.86
		0.3	0.30	0.33	1.04		0.89
	10	1.83	2.30	2.65	3.36	4.39	4.85
		0.3	0.29	0.27	0.82	0.54	0.78

1988; Laruhin et al., 2002). Well-grounded simulation of glow centers in zircon requires, however, the examination of both intra- and interband electron processes. Taking into account high values of the band gap (more than 4−5 eV) characteristic of silicate minerals, such special investigations may be performed only with SR. Nevertheless, SR-induced zircon luminescence has not been previously reported. Note that study of the optical properties of orthosilicates, including zircon, is topical because of probable application of these matrices in optoelectronics.

The objective of this study is to examine the luminescence properties of natural zircon by its selective SR excitation with energy from the visible to soft X-ray region and temperatures from room to helium, and to investigate the glow, reflectance, and excitation luminescence spectra and kinetics of afterglow in a primary crystal and after its oxidative annealing under laboratory conditions. The samples are two single crystals of highly crystalline zircon from the Mir kimberlitic pipe, Yakutia: (1) a primary crystal containing growth defects and affected by autoradiation (zircon I) and (2) a crystal annealed under laboratory conditions in air at 1200°C for thermal recovery of its crystal structure, i.e., healing of growth and radiation defects (zircon II).

EXPERIMENTAL

Measurements were performed on the DORIS, HASYLAB synchrotron, Hamburg, Germany. At the SUPERLUMI station (Zimmerer, 1991), luminescence was induced by VUV radiation (5−21 eV) via a vacuum monochromator (spectral resolution 0.32 nm with a photon energy of 10 eV). The spectra of synchrotron luminescence (SL) in the region of 2.5 to 6 eV were recorded with an R6358P Hamamatsu photomultiplier via an ARC SpectraPro-308i monochromator (grid 300 lines/mm, width of slit 1 mm, maximum sensitivity in the region of 500 nm, Fig. 1). In a BW3 beamline (Larsson et al., 1994), zircon was excited by soft X-ray radiation (50−200 and 500−

620 eV); a Zeiss SX700 monochromator was applied to monochromatize radiation; the luminescence spectra were measured by the second monochromator and photomultiplier on an MCP 1645 Hamamatsu microbeam plate. The SL spectra are given in this paper without correction, whereas the spectra of synchrotron-excited luminescence (SEL) were corrected for the equivalent number of arriving photons. The SL and SEL spectra were recorded both with time integration of the SR pulse and in the time resolution regime; the time resolution of the recording system was about 0.2 ns and determined largely by an effective SR pulse duration of 207 ns. The beam-repetition interval in the DORIS synchrotron ring (912 ns in our runs) has determined the upper limit of the recorded glow kinetics. The reflectance spectra (RS) were measured simultaneously with SEL at an angle of arrival of the SR of about 17.5°. The SR beam aperture was 3 × 0.5 mm. To eliminate the contribution of luminescence to the reflectance spectra, the latter were recorded in the speed time slot. The studied sample was placed in a working chamber with an ultrahigh vacuum of 10^{-8} Pa; the sample was cooled by helium vapor; spectra were recorded at 10 and 300 K.

RESULTS AND DISCUSSION

Luminescence spectra excited by SR with an energy of 6.89 eV; effect of measurement temperature. The SL spectra of zircon I and II at 300 and 77 K and their resolution into individual Gaussian components with a synchrotron excitation energy of 6.89 eV are given in Figs. 1a, 1b, 1d, and 1e. This energy has been chosen, because it is somewhat higher than the published gap values (E_g) of zircon (Demiray et al., 1970; Krasnobaev et al., 1988; Robertson, 2002). At such a high-energy excitation, a rather complex superposition of excitation dispersal processes via both intracenter and interband transfers should be achieved. Indeed, numerous broadband luminescence centers (LCs) (see table) combined into three major groups—ultraviolet LCs A_2 and A_1 (E_{max} = 4.3−4.5 and 4.7−5.0 eV),
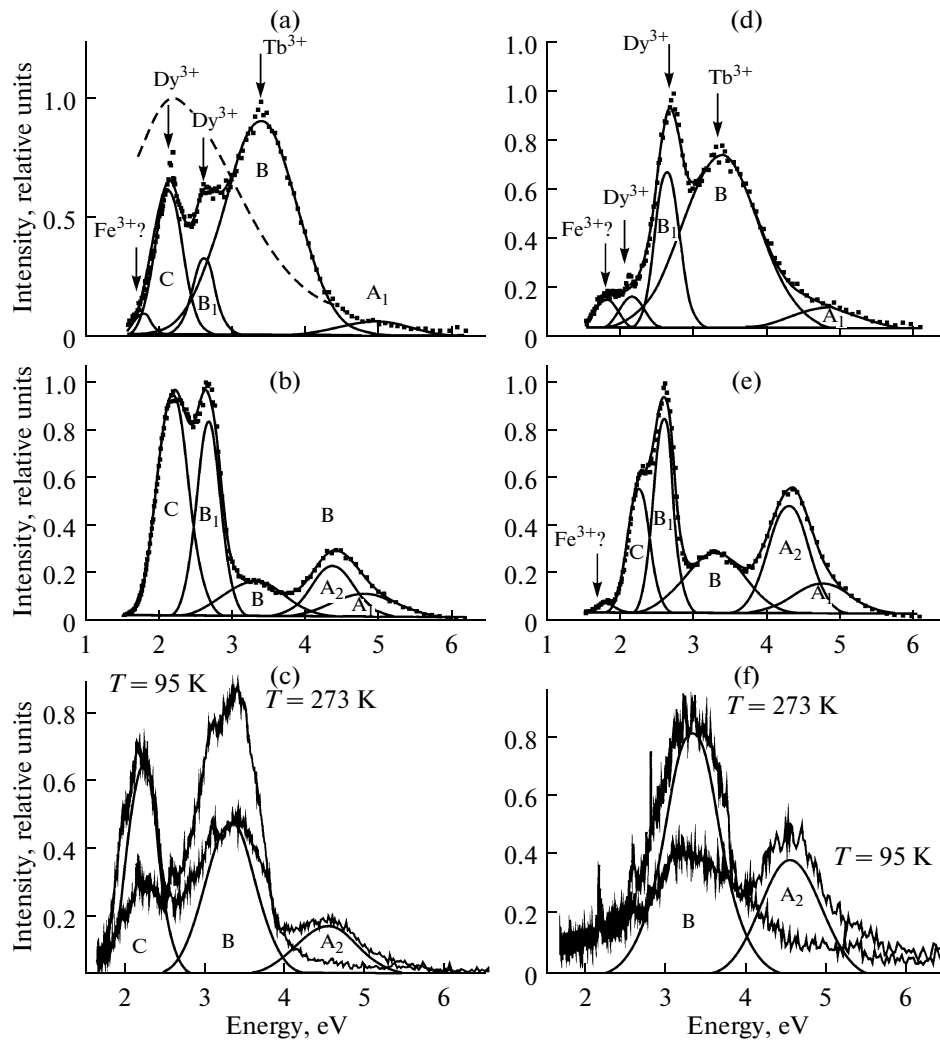
Fig. 1. (a, b, d, e) Luminescence spectra excited by synchrotron radiation with energy of 6.89 eV and (c, f) X-ray radiation and their resolution to the Gaussian components in (a, b, c) zircon I and (d, e, f) zircon II. $T = 300$ K (a, d), 10 K (b, e), and 273 K (c, f). URS-55 is the source of X-ray radiation (voltage 45 kV, current 10 mA). The dashed line is the function of transmission of an ARC SpectraPro-308i monochromator.

blue−green LCs B1 and B ($E_{max} = 2.6$−2.7 and 3.3−3.5 eV), and yellow LCs C ($E_{max} = 2.1$−2.3 eV), have been distinguished in the SL spectra of zircon I and II; herein, LCs are designated after Krasnobaev et al. (1988). In addition to the listed high-intensity bands, a weak band in the near IR region (1.7−1.8 eV, further LC D) is recorded; Gaft et al. (1987) and Nasdala et al. (2002) reported such a band in laser- and cathodoluminescence spectra and suggested its relation to Fe^{3+} impurity ions. Narrow glow bands in the region of 2 to 5.5 eV typical of most zircons and resulting from f−f transitions of REE^{3+} impurity ions are exhibited in the SL spectra only at 300 K; all of them are weak apparently due to both excitation of the matrix by SR with an energy of 6.89 eV and low (approximately 10 nm) resolution of the recording path tuned to measure broad glow bands. Note that rather similar spectra of zircon I and II were observed from other high-energy,

particularly X-ray, excitation (Figs. 1c, 1f), although their intensity was much lower.

The zircon I and II SL spectra indicate that their shape and band parameters (see table) substantially depend on the measurement temperature and thermal history of samples. At 300 K, the spectra of zircon I and II are dominated by LC B (Figs. 1a, 1d), which is typical of their X-ray luminescence spectra (Figs. 1c, 1f); the peak of the LC B band in zircon I slightly shifts to the high-energy region in comparison with zircon II; strong LC C is detected in zircon I, whereas in zircon II it is not recorded. The luminescence center A_1 is established in the spectra of both samples as the high-energy portion of band B; its relative intensity is low (partially because of understated brightness of luminescence in the far UV region due to application of a visible range monochromator in the recording path). Figure 1 demonstrates that temperature

decreasing from 300 to 10 K brings about a significant decrease in glow intensity of LC B and an increase in brightness of LC C and B_1 in the SEL spectra of zircon; in this case, LC C in the spectrum of zircon I becomes predominant. In addition, LC A_2 appears at 10 K. With decreasing temperature, peaks and half-widths of glow bands change (table): band C shifts to the high-energy region; in contrast, band B shifts to the low-energy region and significantly narrows. At 10 K, the contribution of band D to the total photosum of zircon II notably decreases. The luminescence centers A_2 in zircon I and II at 10 K are close in spectral parameters, but in zircon II, they are higher in intensity.

It is known (Nasdala et al., 2002; Ewing et al., 2003) that annealing of zircon induces a number of physical processes, in particular, recrystallization of damaged areas, annealing of growth and radiation defects, healing of oxygen (cation) vacancies, and migration and recharge of impurities. The probabilities of these processes depend on the initial structure, impurity composition, and annealing regime. Recall that zircons from kimberlite are characterized by rather high degrees of sterility and crystallinity, owing to the low dose of autoradiation damage; nevertheless, annealing in air at 1200°C significantly affects their luminescence properties; in particular, the intensity of LC B decreases, although the latter is commonly related to radiation damage to the structure (Votyakov et al., 1986; Remond et al., 1992, 2000; Kempe et al., 2000; Nasdala et al., 2002). It has been suggested that luminescence centers C are related not only to radiation but also to growth defects and their decrease after annealing of kimberlite zircon reflects healing of such defects, vacancies, and local distortions of polyhedrons. In contrast, the effect of high-temperature annealing of zircons on the brightness of LC B is less important, although LC B is a certain oxygen-deficient center associated with Ti impurity (Krasnobaev et al., 1988). In this case, the brightness of the LC B glow is established as significantly affected by temperature: cooling from 300 to 10 K induces its decrease, which may be caused by the thermal stage of excitation of this LC and/or involvement of other defects in glow, whose concentration substantially drops when temperature is decreasing. The competitive capture of carriers by other LCs at low temperature cannot be ruled out either. The predominance of LC A_2 in the spectrum of annealed zircon indicates the increasing efficiency of its glow in the matrix of a more perfect structure.

Thus, SR with an energy of 6.89 eV excites the most known LCs in zircon rather efficiently; comparison of primary and annealed zircon provides evidence for a significant change in the luminescence properties during annealing.

Estimation of the gap value in zircon. The detailed description and understanding of recombination pro-

cesses in zircons require information on the gap value and the electron structure of boundaries of allowed valence and conduction bands. Such experimental data are limited and controversial. The energy of the self-absorption limit of zircon was estimated by Krasnobaev et al. (1988) from the inflection point of the spectral absorption curve for the purest natural zircons from kimberlite at 5.70 eV. The band at 4.71 eV superimposed on the self-absorption limit in the spectrum was assigned by Fielding (1970) to transitions with charge transfer in uranium impurity complexes. In contrast, Taran (1979) attributed this band to the absorption of holes on intrinsic defects of SiO_4^{3-}. According to Demiray et al. (1970), the E_g value estimated from the reflectance spectra of powdered synthetic zircons is 5.95 eV; the absorption band at 4.65 eV was assigned to d–d transitions in the crystal field of vanadium ion. These E_g values differ from the much lower self-absorption values of 4.09 eV published by Richman et al. (1967) and 4.34 eV by Nasdala et al. (2002). According to Robertson (2002), the gap value of zircon is 6.5 eV. As follows from our computation of the zircon electron structure (Shchapova et al., 2005), self-electron transitions O2p $\longrightarrow$ Zr4d start at 5.3 eV; the calculated value of transition energy of the first notable density peak of oxygen states yields 6.6 eV. There are no experimental data on the effect of radiation damage on the value of the energy slot; Nasdala et al. (2002) suggest that radiation damage to the structure of zircon makes it possible to expect a shift in the absorption limit from the near-UV to the visible region of the spectrum.

The classic experimental estimate of the band gap of the crystal implies examination of the thermal behavior of the long-wavelength basic absorption limit using the Urbach rule (Moser, Urbach, 1956). The band gap may be approximately estimated from the reflectance or self-luminescence excitation spectra of the crystal. As is seen from Fig. 2d, showing the reflectance spectrum of zircon I at 10 K, reflectance starts to increase at 5 eV; small inflection at 6.3 eV has also been recorded; the first peak is observed at 7.1 eV. It is known that narrow bands of RS in wide-slot dielectrics may correspond to the generation of excitons; such reflectance is characteristic of crystalline quartz (Silin and Trukhin, 1985). In complex oxide crystals with a low-symmetry oxygen sublattice, exciton reflectance may be exhibited as broad bands because of strong exciton–phonon interaction; for example, such behavior is characteristic of synthetic oxy-orthosilicates (Ivanov et al., 2008). By analogy with oxy-orthoslicates, the RS peak at 7.1 eV was interpreted as the exciton reflectance band of zircon.

We estimated the gap value of zircon from the threshold energy of luminescence excitation at 10 K in the highest energy band A_1 (Figs. 2d, 2h). It is suggested that the glow in this band has its own character and is excited by interband electron transitions with an energy of about E_g. This suggestion is based on the
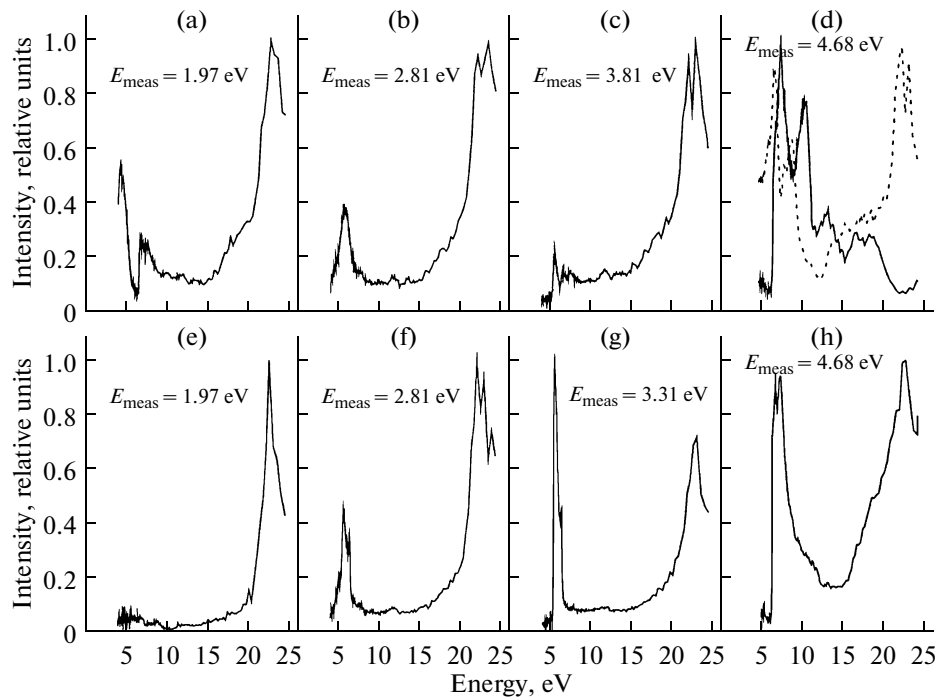
Fig. 2. Excitation spectra of synchrotron luminescence (solid lines) in bands of LC (a, e) C (E_{meas} = 1.97 eV), (b, f) B1 (E_{meas} = 2.81 eV), (c, g) B (E_{meas} = 3.81 (c) and 3.31 eV (g), (d, h) A_1 (E_{meas} = 4.68 eV) and reflectance spectrum (dotted line) of (a–d) zircon I and (e–h) zircon II. T = 10 K.

model of LC A_1, according to which the glow at 4.86–4.68 eV is related to localization of excitons on defect dodecahedrons of ZrO_8. The SEL spectra in the band A_1 start in the region of 6.6 and 6.4 eV for zircon I and II, respectively. The first sharp maximum of the SEL spectra for zircon I corresponds to 7.8 eV (also, there is inflection at 6.8–7.1 eV); for zircon II, sharp maximums are recorded at 7.1 and 7.8 eV. These results allow us to estimate the excitation energy of exciton glow at 7.1 eV.

Thus, the available data show that the beginning of basic absorption of zircon corresponds to energies of 6.4 to 6.6 eV; the excitation that presumably resulted from exciton generation corresponds to 7.1 eV. Since the energy of exciton absorption, as a rule, is somewhat below the E_g value, it can be suggested that the true gap value is slightly higher than 7.1 eV.

Luminescence spectra excited by SR with an energy above and below band gap of zircon. The luminescence spectra of zircon I and II with different energy of exciting SR relative to gap value ($E_{excit} \ll E_g$, $E_{excit} \sim E_g$, and $E_{excit} \gg E_g$) are shown in Figs. 1, 3, and 4. The comparison of the spectra shows significant change of their pattern with changing excitation energy, in particular, for zircon I at E_{excit} = 4.42 eV < E_g, LC C and B_1 glow; at E_{excit} = 6.20 eV, LC C, B_1, B, and A_2; and at E_{excit} = 6.89 eV ~ E_g, LC C, B_1, B, A_2, and A_1. Centers C, B_1, B, and A_2 excited by SR of $E_{excit} < E_g$ should be related to the intrinsic (impurity) defects of the zircon structure forming levels in the band gap, whereas

LC A_1 excited by SR of $E_{excit} \sim E_g$ may have another nature. It is established that the peak position and halfwidth of bands attributed to structural defects depend on the energy of the exciting SR. In particular, with an increase in E_{excit} from 4.2 to 6.89 eV, the band of the LC C shifts from 2.13 to 2.22 eV and E_{excit} increases from 6.20 to 6.89, inducing a shift of LC B_1 and B from 2.46 to 2.69 eV and from 3.13 to 3.31 eV, respectively. It can be suggested that the observed effect is a consequence of some distribution of defect levels by energy owing to scattering of short-range-order parameters in the defect crystal. The luminescence centers D, B_1, and B glow in zircon II excited by SR with E_{excit} = 5.64 eV < E_g; excitation with E_{excit} = 6.89 eV ~ E_g results in glow of LC D, C, B_1, B, A_2, and A_1. The LC C in zircon II with E_{excit} = 5.44 eV < E_g is not displayed, but it has been recorded at E_{excit} = 6.89 eV ~ E_g. The peaks of luminescence bands in zircon II are shifted to the region of high energy with increasing energy of exciting SR, although this effect in zircon II is less pronounced because of higher structural ordering of this zircon.

During SR excitation with $E_{excit} \gg E_g$, LC A_1 (peak at 4.76 eV, halfwidth 0.8 eV) and A_0 (peak at 5.41 eV, halfwidth 0.5 eV) glow; note that the latter was not reported previously. It was established that the increase in energy of exciting SR from 130 to 560 eV brings about increasing intensity of LC A_1 and A_0; they become predominant in spectra, indicating the intrinsic nature of these centers. Note that LCs A_1 and A_0
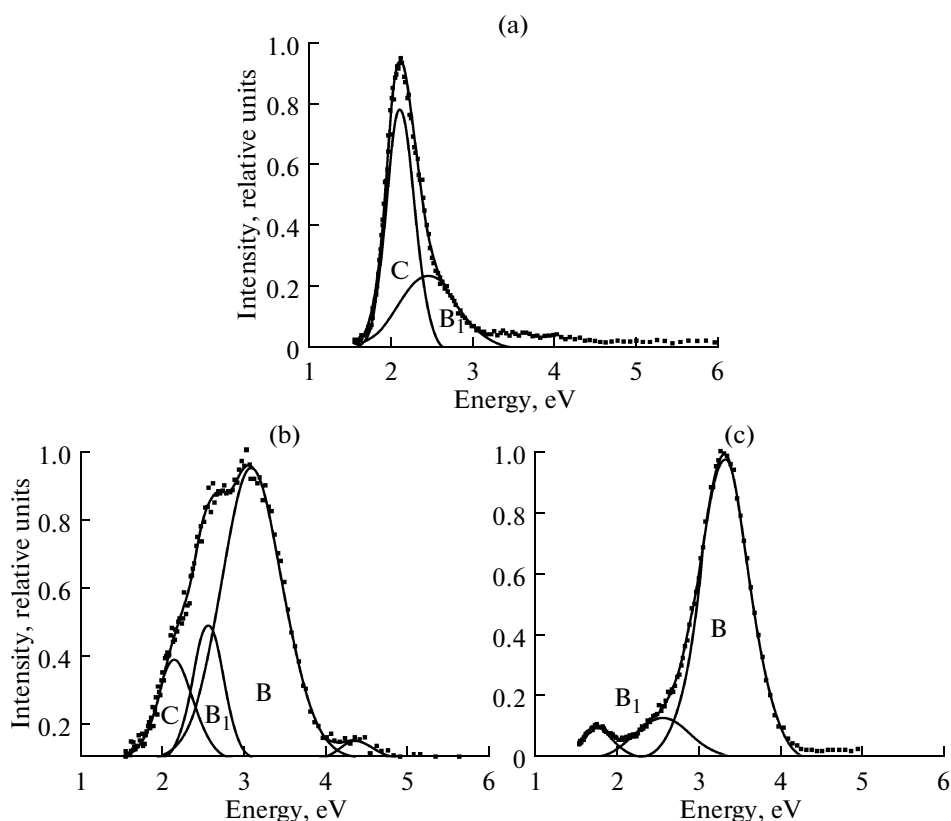
Fig. 3. Synchrotron-excited luminescence spectra of energy, eV: (a) 4.42, (b) 6.2, and (c) 5.64 in zircon (a, b) I and (c) zircon II; $T = 10$ K.

differ in the damping kinetics : the exponent component with a response time about 0.5 ns is detected in the afterglow of LC A_0; in contrast, damping in the microsecond range is characteristic of LC A_1. The presence of two intrinsic glow bands of different damping kinetics is typical of complex oxides, particularly orthosilicates (Ivanov et al., 2005, 2006, 2008), and may be regarded as a manifestation of various relaxation channels of electron excitations in crystals with complex structure of the oxygen sublattice.

Thus, selective excitation of zircon by SR of different energies relative to E_g allows dividing all detected LCs into those related to the glow of defects (LC C, B_1, B, and A_2) and intrinsic glow of the matrix (LCs A_1, A_0) probably with the participation of excitons. The shift of glow bands of C, B_1, and B to the high-energy region of exciting SR is established; this shift decreases after oxidative annealing of the sample.

Excitation spectra of broadband luminescence centers and their structural models. Interpretation of the nature of broadband LCs A−C in zircon is ambiguous. Iacconi et al. (1980) suggested that blue broadband luminescence (peak at 3.4 eV, apparently, LC B) like in other silicates is related to the glow of the electron center on the SiO_4 tetrahedron (Si^{3+} center) (Yang et al., 1992; Kempe et al., 2000) probably stabilized by

impurities (Gaft, 1992; Claridge et al., 2000a). The latter suggestion is consistent with the hypothesis that both centers on SiO_4 tetrahedrons and REE are involved in thermoluminescence with a peak at 3.2 eV (Kirsh and Townsed, 1987; Laruhin et al., 2002). From a comparison of EPR data and relationships between the concentration and intensity of X-ray luminescence in synthetic zircon crystals doped by Ti, Krasnobaev et al. (1988) suggested that LC B results from isomorphic substitution of Zr^{4+} for Ti^{4+}. In most studies, yellow luminescence (LC C) was attributed to radiation damage to the structure (Votyakov et al., 1986; Krasnobaev et al., 1988; Gaft, 1992, 2002; Remond et al., 1992,2000; Kempe et al., 2000, Nasdala et al., 2002). The first of the cited papers argues for the relation of the center to the SiO_3^{3-} and SiO_2^{-} defect clusters (mono- and divacancy of oxygen); the model of LC C as electron centers on SiO_4 tetrahedrons stabilized by Zr vacancies was proposed by Claridge et al. (2000). Gaft et al. (2002) revealed that in natural and synthetic samples irradiated with α-particles, the peak in the photoexcited spectra of LC C corresponds to 4 eV, and damping response time, to 25–35 μs; the authors did not discuss a physical model of LC C. Krasnobaev et al. (1988) and Gorobets and Rogozhin (2001) suggested the intrinsic nature of LC

A_1 and A_2. We have studied the SEL spectra of the aforementioned LCs in zircon to furnish additional evidence for their nature (Fig. 2).

Luminescence center C in zircon I is efficiently synchrotron excited in bands of 4.4 and 6.9 eV; in contrast, the efficiency of its excitation in zircon II is extremely low (Fig. 2a, 2e), clearly indicating its relationship to intrinsic defect structural fragments of growth (radiation) nature, which are healed in the course of annealing. The spectral parameters of LC C are sufficiently close to those of intrinsic LC on non-bridge oxygen (O_1^0 or NBOHC center) in quartz glasses and crystalline quartz irradiated by neutrons (Silin and Trukhin, 1985; Skuja, 1998). Recall that in the glow spectra of the NBOHC center in quartz, a peak at 1.85–1.95 eV is distinguished; its afterglow damping response time is 10–20 μs; the peak at 4.8 eV is predominant in the excitation spectrum of the center (the second low-intensive peak is at 2.0 eV). It is supposed that the NBOHC center in quartz results from hole trapping by oxygen ion in the presence of the broken bridge bond Si–O–Si. In the structure of zircon, all oxygen anions of isolated SiO_4 tetrahedrons are triple-coordinated $Si-O_{-Zr}^{-Zr}$. This allows us to suggest that the fragments where O–Zr bonds are broken because of the formation of Zr vacancies (or strong distortion of ZrO_8 and SiO_4 polyhedrons with increasing Zr–O distances and the appearance of irregular nonbridge bonds Si–O) are analogues of the NBOHC center in zircon. Note that Zr vacancies and structural distortions are actually formed as a result of metamict alteration of zircon and radiation expansion of its structure (Ewing et al., 2003). The stable centers arising due to hole capture by tetrahedrons situated close to the Zr vacancy are well known from EPR data. The difference in the spectroscopic parameters of the NBOHC center and LC C (the absorption band of the latter is shifted to the lower energy region, and the Stocks shift is reduced) is explained by the different electron structure of SiO_4 tetrahedrons in zircon and quartz, in particular, by the distinct spectrum of electron 2p states of bridge Si–O–Si and triple coordinated $Si-O_{-Zr}^{-Zr}$ oxygen atom (Shchapova et al., 2005). Thus, one of the probable intrinsic structural defects responsible for the appearance of LC C and its peak in the SEL spectrum with $E_{excit} = 4.4$ eV is a distorted SiO_4 tetrahedron associated with a Zr vacancy. The previously reported nonelemental nature of the LC C band recorded in the presence of a few components with a different response damping time and thermostability (Gaft et al., 1987; Krasnobaev et al., 1987) may be related to distinct ways of charge compensation of a tetrahedron that trapped a hole in zircon. The second detected peak (6.9 eV, Fig. 2) in the SEL spectrum of LC C is close to E_g of zircon; i.e., it may be
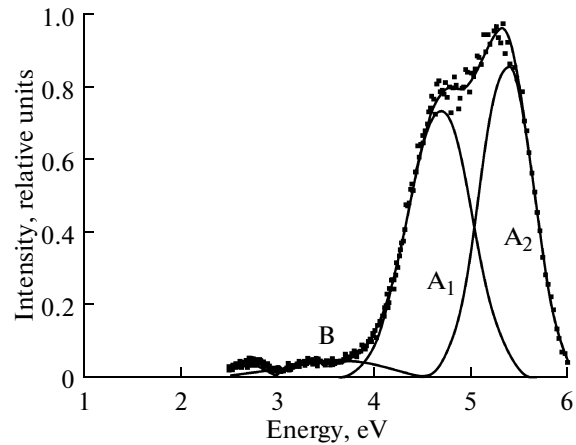

Fig. 4. Synchrotron-excited luminescence spectrum of zircon II with SR energy of 130 eV; $T = 10$ K.

suggested that LC C is probably excited as a result of interband (basic) absorption.

The LC B_1 in zircon I is synchrotron-excited in the band of 5.8 eV and in bands of 5.9 and 6.6 eV in zircon II (Fig. 2). Note that an LC with close spectral parameters ($E_{rad} = 2.7$ eV) is well known for crystalline and amorphous silica; it is attributed to the oxygen-deficient centers ODC(II)—vacancies and divacancies of oxygen—in the mineral. This LC in quartz is excited as bands at 3.15, 5.0, and 6.9 eV; its response damping time is 10.2 ms; there is a second band of quick de-excitation at 4.3 eV with a response time of 4 ns; the denoted glow bands are assigned to the triplet–singlet and singlet–singlet transition (Silin and Trukhin, 1985), respectively. Double-coordinated silicon $Si_2^{\cdot 0}$ or the neutral oxygen vacancy between neighboring Si atoms are considered models of the center in quartz. Skuja (1998) showed the possibility of mutual conversion of these defects as a result of photostimulated processes with the participation of the crystal sublattice. It is evident that oxygen-deficient centers similar to those in quartz occur in zircon having growth (radiation) defects; the parameters of corresponding paramagnetic centers were described from EPR data (Krasnobaev et al., 1988; Claridge et al., 2000). At the same time, a discrepancy between bands in the SEL spectra of LC B_1 and those in the excitation spectrum of oxygen-deficient centers in quartz does not allow their direct correlation and requires additional investigation.

The LC B is characterized by an excitation spectrum nearly identical to that of LC B_1 (Fig. 2), indicating the common initial stage of their excitation. Krasnobaev et al. (1988) reported correlation between LC B (and B_1) glow and the concentration of Ti; this gives grounds to suggest that LC B is a certain oxygen-deficient center associated with Ti and related to thermal energy transfer to the luminescent level (recall that LC

B is characterized by a decrease in brightness of its luminescence with temperature drop, indicating that thermal stage of the center excitation does exist).

The LC A_1 is synchrotron-excited as bands of 7.1, 7.8, 10.6, and 13.5 eV in zircon I and as bands of 7.1 and 7.8 eV in zircon II (Fig. 2). This LC is probably related to the glow of excitons excited in the region of the self-absorption limit (7.1 and 7.8 eV); this suggestion is supported by LC A_1, detectable only at low temperature and increasing intensity of LC A_1 with an increase in the energy of exciting SR. Krasnobaev et al. (1988) and Gorobets and Rogozhin (2001) assumed the exciton origin of LC A_1. Note that LC A_0 induced by soft X-ray radiation can also be of exciton nature. The additional peaks at 10.6 and 13.5 eV are a distinctive feature of the SEL spectrum of LC A_1 in zircon I. Recall that the appearance of some bands in the absorption spectrum of quartz with an energy higher than 10 eV (10.4, 11.6, and 14.4 eV) is caused by the creation of autolocalized excitons of three types (Silin and Trukhin, 1985). These bands are characteristic of the structure of silica containing bridge oxygen atoms and distinguished by a higher degree of connectivity of the SiO sublattice in comparison with orthosilicates. Therefore, the SEL spectrum of zircon I evidences the presence of polymerized areas in the mineral structure arising, for instance, as a result of convergence of SiO_4 tetrahedrons and the formation of vacancy defects of growth (radiation) nature. Similar additional bands in the excitation spectra appearing in the Y_2SiO_5–Lu_2SiO_5–Sc_2SiO_5 orthosilicate series were interpreted as the effect of convergence of SiO_4 tetrahedrons due to a decrease in size of REE cation (Ivanov et al., 2008). The absence of additional bands in the SEL spectrum of zircon II is consistent with recovery of the zircon structure with isolated SiO_4 tetrahedrons during high-temperature oxidative annealing.

CONCLUSIONS

The luminescent properties of two single zircon crystals from kimberlite were studied at 300 and 10 K, and their selective synchrotron excitation with an energy ranging from visible to soft X-ray; the spectra of glow and major excitation bands were examined; the physical nature of luminescence centers is considered; and the luminescent properties of the crystal containing growth and radiation structural defects is compared with a crystal that initially contained the same impurities and then thermally recrystallized. The zoned structure of zircon crystals is examined, and the gap value of the mineral ($E_g = 7.1$ eV) is estimated. Selective excitation of zircon with different synchrotron energies relative to the gap value ($E_{excit} < E_g$, $E_{excit} \sim E_g$, and $E_{excit} \gg E_g$) was used for subdivision of luminescence bands into two groups: (1) related to impurities of intrinsic (growth, radiation) nature ($E_{max} = 2.1$, 2.7–2.8, and 3.2–3.3 eV) and (2) matrix luminescence ($E_{max} = 4.4$–4.7 and 5.4 eV) probably with the participation of excitons. The short-lived component with a response time of 4 ns was revealed in the afterglow of zircon in the region of 5.4 eV.

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