

Laser-induced time-resolved spectroscopy of visible broad luminescence bands in zircon

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Summary

This work examines the luminescence of zircon studied by laser-induced time-resolved methods. This method allows the differentiation between luminescence centers of similar emission wavelengths, but different decay times. Samples include a suite of natural zircons, nominally pure synthetic ZrSiO₄, and ZrSiO₄ artificially doped by Mn, Fe, Cr, Ni, Co, Pb, Sb, Ti, Ta, V, Sc, U, U-P, and Th-P. In addition, pure ZrSiO₄ samples irradiated by thermal neutrons have been studied.

We have clarified the nature of several luminescence bands reported previously from time independent studies, and suggest the following as the causes of luminescence in zircon systems: 1) the yellow band with peak wavelength (λ_{\max}) = 575 nm, peak half-width (Δ) = 120–130 nm, and decay time (τ) = 30–35 μ s is connected with neutron and alpha irradiation, 2) the green band with λ_{\max} = 505 nm and vibrational structure is linked to the presence of the uranyl ion, but it is only observed in artificial samples with co-doping by U and P, 3) the red band with λ_{\max} = 750 nm, Δ = 110–120 nm and τ = 3–5 ms is connected with Fe³⁺. We have also identified new luminescence bands, obscured by stronger emissions. These are: emission a) with λ_{\max} = 480 nm, Δ = 70–80 nm and τ = 300–325 μ s, emission b) with λ_{\max} = 515 nm, Δ = 90–100 nm and τ = 500–520 μ s, emission c) with λ_{\max} = 605 nm, Δ = 110–125 nm and τ = 8–10 μ s. These emissions have not been detected in synthetic doped zircons and their interpretation remains the subject of further investigation.

Introduction

Zircon is a zirconium silicate, ZrSiO_4 , with a tetragonal structure (Space Group: $I4_1/amd$), in the unit cell of which there are four SiO_4^{4-} tetrahedra and four ZrO_8^{12-} dodecahedra. In nature, zircon is an accessory mineral found almost ubiquitously in igneous, sedimentary and metamorphic rocks. The crystal chemistry of zircon strongly favors the incorporation of REE in the Zr^{4+} site. The REE impurities become luminescent in the crystallographic environment of the lattice and their laser-induced time-resolved luminescence has been recently investigated (Gaft et al., 2000a).

Besides REE, broad spectral bands in the yellow–green part of the spectrum characterize the luminescence of zircon. They are structureless down to 4.6 K, which provides little insight into the nature of the luminescent centers. Previous work has made a variety of suppositions and even the question of whether yellow luminescence is related to an intrinsic or impurity defect remains open. For example, the yellow band (“C-band”) was ascribed to $(\text{SiO}_m)^{n-}$ defects (Krasnobaev et al., 1988; Votyakov et al., 1993), while the same emission (“band VII”) was explained by an impurity-related luminescence, namely by Yb^{2+} created by the radioactive reduction of Yb^{3+} (Kempe et al., 2000).

It has been proposed previously that yellow zircon luminescence is connected not with one, but with many centers, each of which have similar luminescence and excitation spectra but different decay times and thermal stability (Shinno, 1986; Gaft et al., 1987; Gaft, 1992). For these reasons, spectroscopic methods alone are not sufficient to resolve the broad spectra into individual bands. The present study examines a variety of zircon samples by laser-induced *time-resolved* luminescence, which allows differentiation between luminescence centers with emissions of similar wavelengths but with different decay times. This method involves recording the luminescence spectrum in a specific time gate at a given delay after the excitation pulse. Both the delay and the gate width have to be carefully chosen in order to be suitable for specific decay time of the corresponding luminescence center. To ensure the correct interpretation of the luminescent bands, artificial zircon standards have also been investigated, including a nominally pure ZrSiO_4 , as well as zircons doped by different potential luminescent impurities.

Experimental

The luminescence spectra were investigated under third and fourth harmonic of YAG (355 and 266 nm), excimer (308 nm) and nitrogen (337 nm) laser excitations, which deliver pulses of 10 ns duration and 0.1 cm^{-1} spectral width. The pulse energy was maintained to about 40 mJ for 308 and 355 nm and 10–15 mJ for 337 and 266 nm. The spectra were observed at a geometry of 90° from the primary laser pulse and were collected by an InstaSpec V (Andor). This equipment enables time-resolving spectral acquisition with delay times and strobe pulse duration of between 20 ns to 9 ms, a spectral wavelength range between 300–900 nm (1200 channels, spectral resolution 0.1–1 nm, gratings with 400 and 1200 lines mm^{-1}) using an intensified CCD matrix detector.

Approximately 50 natural zircons have been investigated. The four representative samples described in this paper contain all the bands detected in present investigations. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analyses allow

Table 1. Concentrations of impurities in investigated zircons (ppm) determined by Inductively Coupled Plasma Mass Spectrometry

	Mn	Fe	Ti	Mo	V	Nb	Ni	Pb	Ta	U
Australia	10	400	1200	0.5	90	20	10	15	4	550
Norway	150	475	120	0.5	3	100	15	8	15	120
Canada	100	2200	75	5	250	20	75	na	20	700
Kola, Russia	40	400	40	2	150	150	30	na	2.5	40

na not analyzed

the compositions of the samples to be determined at ppm precision and those results are presented in Table 1. Synthesis of nominally pure ZrSiO_4 as well as samples doped with Mn, Fe, Cr, Ni, Co, Pb, Sb, Ti, Ta, V, Sc, U, U–P, Th–P was achieved by the flux growth method (Shinno, 1987). All zircons obtained were transparent single crystals about 0.1 mm in size and almost colorless, except for those doped with Nb, Mn, Fe and U. Some synthetic and natural zircons were also irradiated by thermal neutrons (Hayashi et al., 1990). The thermal neutron flux was about from 5.1×10^{11} to 8×10^{13} neutrons $\text{cm}^{-2} \text{s}^{-1}$. The irradiation time ranged from 1–60 min. The internal irradiation with α -particles was performed by the nuclear (n, α) reaction of Ca ions doped in the synthetic zircon crystals (Shinno, 1986).

Results and discussion

Natural samples

Figure 1 presents laser-induced time-resolved luminescence recorded at 300 K from two natural zircons (brown zircon crystals from the Kola Peninsula, Russia and detrital gray zircon from Australia, Table 1) at different excitation wavelength, delay and gates. Such behavior is most typical of zircons. At 266 nm excitation, the spectrum consists of the well-known, yellow, broad, asymmetric band peaking at 575 nm with decay time of approximately 25–35 μs (Fig. 1a). The spectrum is not significantly changed using different delay times and gate widths. After heating the sample to 700 °C the luminescence intensity is nearly the same, but beyond that temperature it is strongly reduced and at 800 °C the yellow luminescence disappears. This observation is connected with the thermal destruction of the corresponding luminescence center. Yellow luminescence does not reappear after heating at higher temperatures up to 1100 °C. Luminescence spectra at 77 K are not significantly different. At 308 nm excitation (Fig. 1b), in addition to the yellow band described above, a new band appears at 480 nm with half-width of 70 nm. This has relatively long decay time of 300 μs and dominates the spectra. At 337 nm excitation (Fig. 1c), another new band appears at 505 nm with half-width of 100 nm with an even longer decay time of $\sim 500 \mu\text{s}$.

Figure 2a represents laser-induced time-resolved luminescence spectra of another zircon (from Norway in Table 1) at 300 K. Such luminescence is very rare. The spectrum at 77 K is much broader compared with that at 300 K and contains an additional orange band to that in the yellow (Fig. 2b). Both bands have similar decay times and are not clearly resolved even by time-resolved spectroscopy. After heating to 800 °C, the yellow band disappears and the orange luminescence is

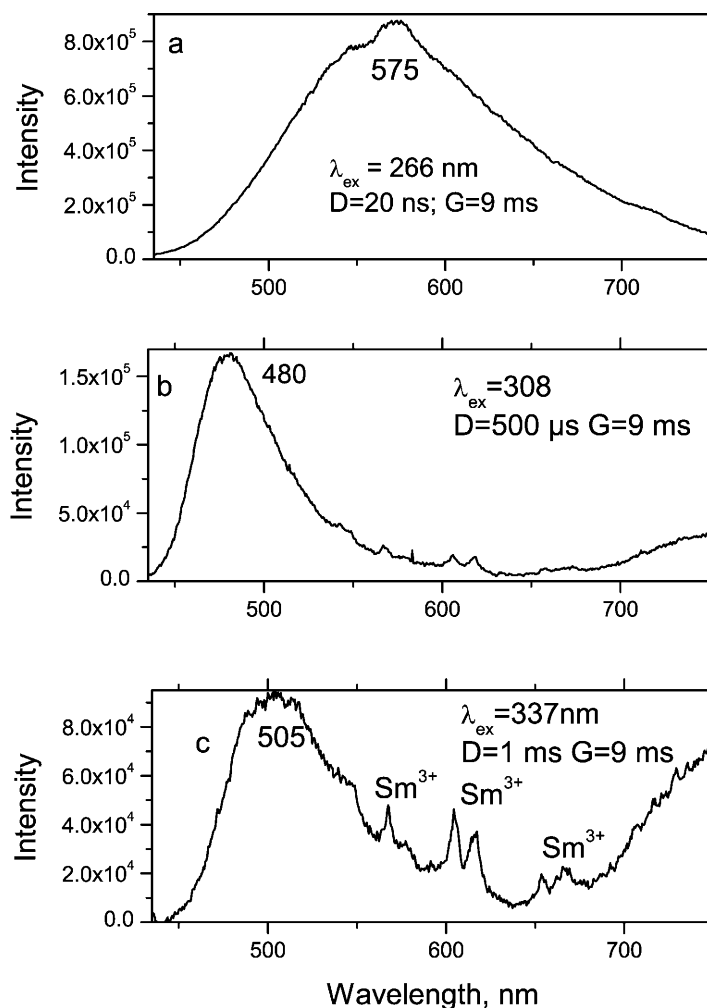


Fig. 1. Laser-induced time-resolved luminescence spectra of natural zircon (Kola): **a** radiation induced band; **b**, **c** luminescence bands with unknown origin

detected at 600 nm with half-width of 125 nm (Fig. 2c,d). It has short decay time of 10 μ s and dominates in those spectra collected with a narrow gate width. The narrow “negative” lines at 658 and 699 nm coincide with the absorption lines of U^{4+} (Gaft et al., 1987).

Synthetic ZrSiO₄

Radiation-induced luminescence. The dominant yellow band at 575 nm with decay time of 25–35 μ s represents “classical” zircon luminescence. Its link to irradiation was first supposed many years ago (Tarashchan, 1978), but, as mentioned above, its origin remains ambiguous. In order to study the influence of irradiation on laser-induced time-resolved luminescence, we investigated the following samples:

- Synthetic $ZrSiO_4$ doped with Eu showing characteristic narrow Eu^{3+} lines, which was then irradiated by different doses of thermal neutrons;

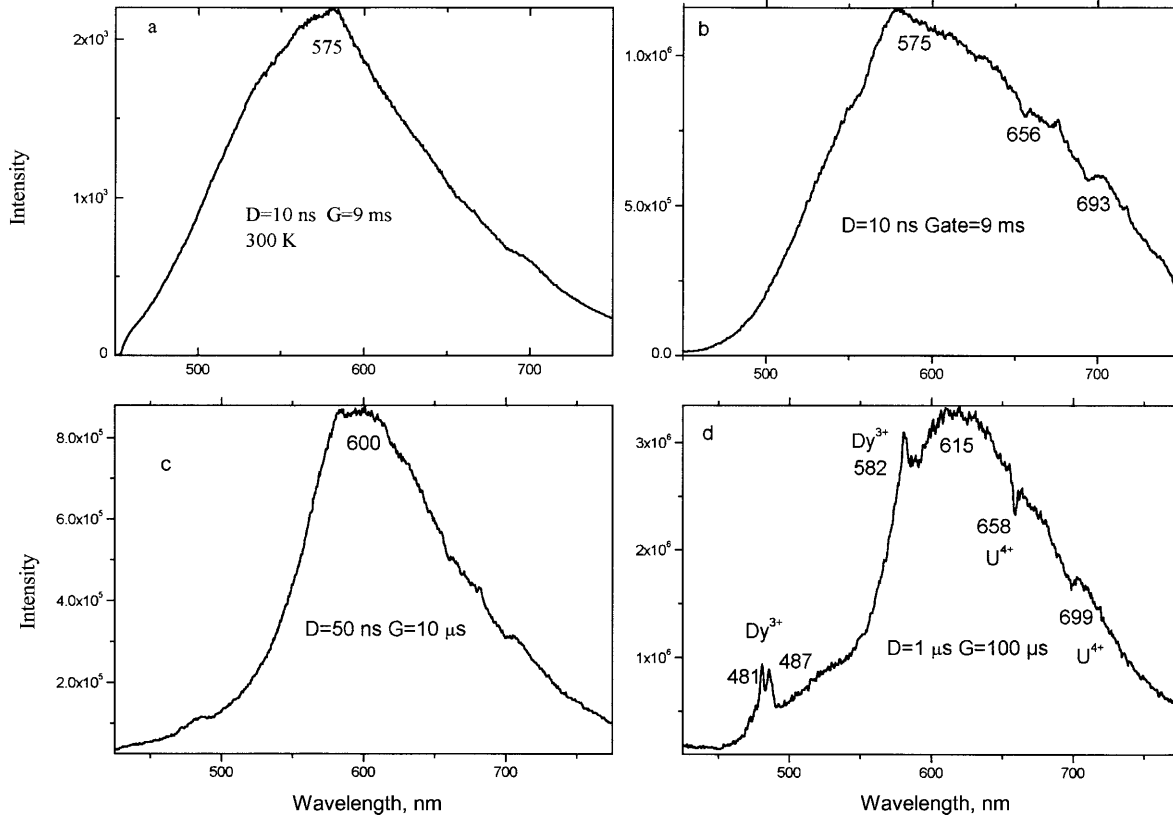


Fig. 2. Laser-induced time-resolved luminescence spectra of natural zircon (Norway) under 337 nm excitation: **a** spectrum measured at 300 K; **b** spectrum measured at 77 K; **c** after heating to 800 °C, spectrum measured at 300 K; **d** after heating to 800 °C, spectrum measured at 77 K

- Synthetic ZrSiO_4 activated by Ca and P initially without luminescence but then subjected to internal irradiation by alpha particles. This was achieved by irradiation by neutrons, which, following the absorption of neutrons by Ca, caused the production of alpha particles;
- Natural zircons annealed at 800 °C for 1 hr (when natural yellow broad band luminescence almost totally disappears) and then irradiated by different doses of alpha particles.

$\text{ZrSiO}_4:\text{Eu}$ which has not been irradiated is characterized by strong orange luminescence (Fig. 3a), linked to two different types of Eu^{3+} centers (Gaft et al., 2000b). After neutron irradiation, the broad yellow luminescence band appears, much more intense than the original Eu^{3+} emission (Fig. 3b). Such yellow luminescence is proportionally stronger with increasing irradiation time. Strong broad band yellow luminescence appears after alpha-irradiation in $\text{ZrSiO}_4:\text{Ca}/\text{P}$ and also in natural zircon after heating at high temperatures (Fig. 3c). Both those samples were not luminescent before irradiation. Investigations made at 300 and 77 K with different laser excitations, delays and gates prove that, despite of very broad half-width and apparently asymmetric form, luminescence consists of only one band.

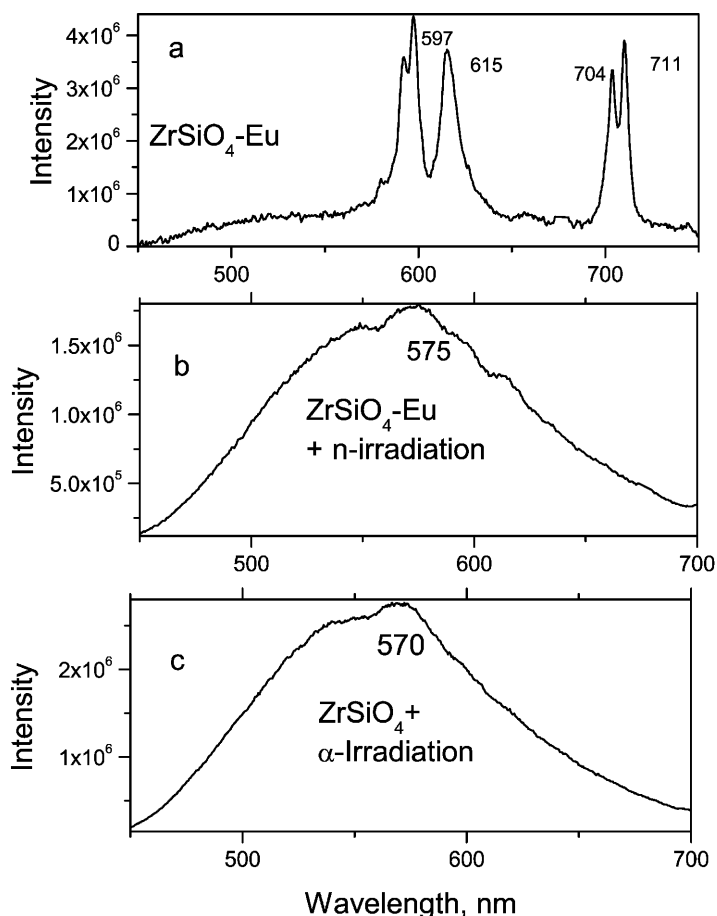


Fig. 3. Laser-induced time-resolved luminescence spectra of ZrSiO₄:Eu (a), alpha-irradiated ZrSiO₄:Eu (b) and non-luminescent ZrSiO₄ after neutron irradiation (c)

For both alpha and neutron irradiation, such induced luminescence is stable with time and in our study has been detected several years after irradiation.

The spectral profile of this radiation-induced luminescence is very close to that of natural zircon samples. Its decay time is $\sim 30\text{--}35\ \mu\text{s}$ and the intensity remains stable when heated to $700\ ^\circ\text{C}$, all of which are characteristic of natural samples. We conclude that the “classical” yellow luminescence band in natural zircon with $\lambda_{\text{max}} = 575\ \text{nm}$, half-width (Δ) = $160\ \text{nm}$, decay time (τ) = $30\text{--}35\ \mu\text{s}$ and thermally stable up to $\sim 700\ ^\circ\text{C}$ is connected with radiation induced centers. In minerals, the source of the irradiation may be the radioactive decay of U and Th impurities.

For the interpretation of such centers it is important to note that yellow luminescence is connected only with neutron and α -irradiation and not generated by high doses of X-rays, nor β - or γ -radiation. Thus, the corresponding centers must be specific only to neutron and α -treatment. According to EPR (Hayashi et al., 1990), neutron irradiation produces four typical signals in ZrSiO₄ with $g = 2.000$, 2.001 , 2.003 and 2.008 , while γ -ray irradiation produces only the first two signals. The last signal is completely extinguished eight months after irradiation, while that

with $g = 2.003$ remains. In our study, laser-induced luminescence is detected even 10 yr after irradiation. We therefore suppose that the luminescence is connected with the radiation-induced center with an EPR signature at $g = 2.003$. Such a value of g corresponds to $(\text{SiO}_m)^{n-}$ structural defects, although its exact nature is not known (Krasnobayev et al., 1988; Votyakov et al., 1992). Nevertheless, our comparison of the thermal stability of the $(\text{SiO}_m)^{n-}$ defects and the yellow luminescence intensities reveal that any correlation is absent (Gaft et al., 1987). Therefore, the exact nature of the yellow luminescence center needs further clarification.

Impurity-related luminescence

The other bands described above do not appear in nominally pure ZrSiO_4 before and after different types of irradiation and may be considered as impurity connected. To elucidate the nature of such luminescence centers, synthetic ZrSiO_4 doped with various elements was studied. Figure 4 demonstrates strong luminescence bands in the visible part of the spectrum received as a result of activation by certain impurities.

Mn^{2+} . The ionic radius of Mn^{2+} (0.97 \AA) is close to those of Zr^{4+} (0.88 \AA) (www.webelements) and the corresponding substitution is possible with proper

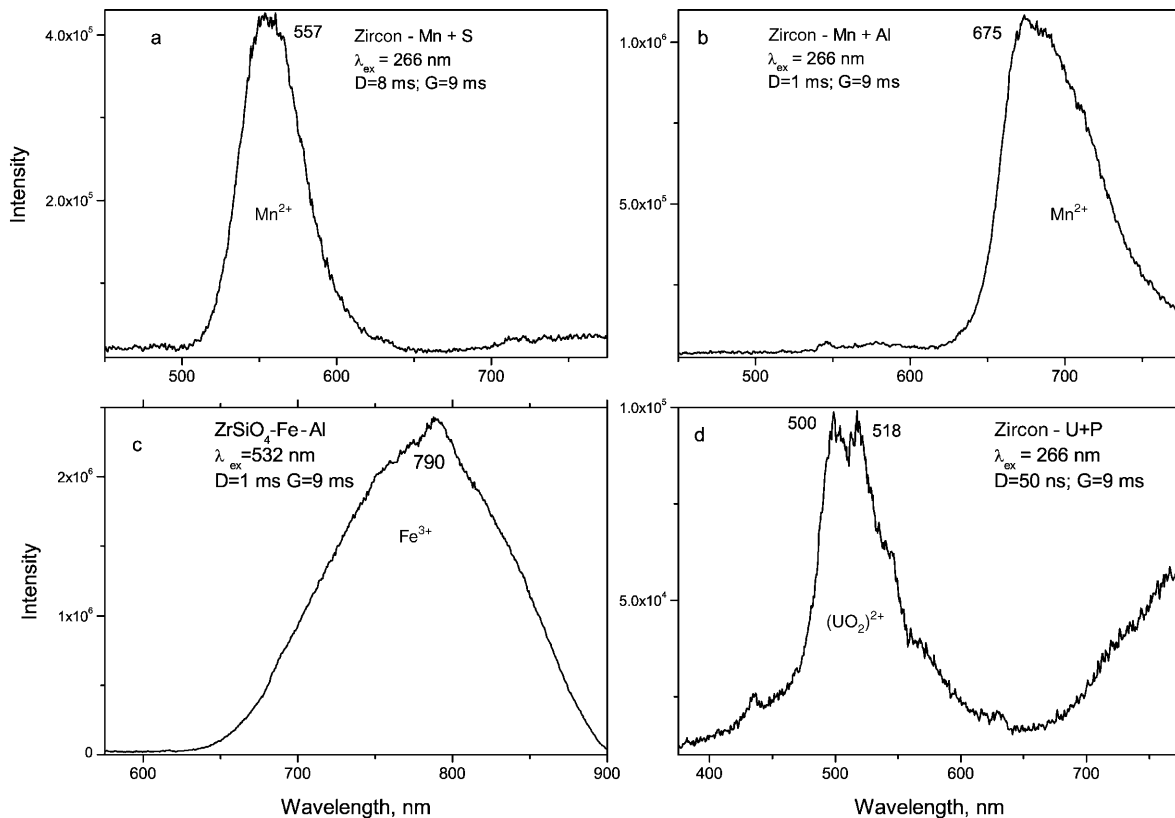


Fig. 4. Laser-induced time-resolved luminescence spectra of ZrSiO_4 activated by Mn (a, b), Fe (c) and Sc/P (d). $\lambda_{\text{ex}} = 266 \text{ nm}$

charge compensation. The presence of Mn impurities in quantities in zircons under investigation was confirmed by ICP-MS analyses (Table 1). In order to check the possible connection between luminescence and Mn^{2+} , ZrSiO_4 activated by Mn was studied. Intensive narrow bands with very long decay times were found with spectral positions strongly depended on co-activator (Fig. 4a,b). Principally, such differences may be connected with several kinds of Mn^{2+} centers with different local symmetry, for example, $\text{Mn}^{2+} - \text{Si}^{4+}$ (tetrahedral) and $\text{Mn}^{2+} - \text{Zr}^{4+}$ (octahedral) substitutions, although the small ionic radius of Si^{4+} of 0.4 Å (www.webelements) makes such substitution very doubtful. In any case, such luminescence bands have never been detected in the luminescence spectra of natural zircons. We suppose that zircon contains Mn not as Mn^{2+} , but as Mn^{4+} , confirmed by EPR (Votyakov et al., 1992). Furthermore, the Mn^{4+} ion is isoelectronic with Cr^{3+} and its luminescence is well known in synthetic phosphors (Blasse and Grabmaier, 1995). The crystal field of the more highly charged Mn^{4+} ion is stronger than Cr^{3+} , so that the Mn^{4+} emission always consists of two sharp lines in the red part of the spectrum. This has not been detected in zircon.

Fe^{3+} . Broad deep red luminescence is detected in many natural zircons. It is thermally stable and dominates in the thermally treated zircons after annealing at 800 °C. The decay time of 1 ms is very long and such an emission is especially evident in spectra with long delay times when the stronger yellow luminescence is already quenched. Such emission is very typical of forbidden d–d transitions in Fe^{3+} . Iron impurities are present in natural zircon (Table 1) and the connection between red zircon luminescence with Fe^{3+} has been proposed (Gaft et al., 1987). Nevertheless, such luminescence was not detected in artificial $\text{ZrSiO}_4:\text{Fe}$ (Krasnobayev et al., 1988). In order to clarify this, we studied artificial $\text{ZrSiO}_4:\text{Fe}$ by laser-induced time-resolved spectroscopy. Deep red broad band luminescence with long decay time was observed, very similar to that in natural zircon (Fig. 4c).

Other potential causes of broadband red luminescence are Ti^{3+} and Cr^{3+} , especially given that they are detected in zircon by EPR (Votyakov et al., 1992) and ICP-MS (Table 1). Red luminescence in zircon sometimes contains a short decay component, characteristic of Ti^{3+} and Cr^{3+} centers (Gaft et al., 1987). We studied the ZrSiO_4 activated by Ti but red luminescence was not detected. Luminescence of ZrSiO_4 activated by Cr is very complicated (Gaft et al., 2000b). Broadband luminescence peaking at 750–770 nm attributed to Cr^{3+} has been detected, accompanied by weak narrow R-lines. Thus participation of Cr^{3+} in the red luminescence of natural zircon is possible.

U-P. Several zircons have strong green luminescence with clear vibrational structure (Shinno, 1987). Such luminescence is usually connected with uranyl (UO_2^{2+}) luminescence centers, specifically with the adsorption of uranyl complexes on mineral surfaces (Gorobets and Rogozin, 2001). Such luminescence can be created artificially in synthetic zircon doped with U and P (Fig. 4d). In synthetic zircons doped with Th and P, and with U only, such luminescence is not obtained. The link between the luminescence and U is confirmed by the correlation between intensity and U contents, determined by ICP-MS (e.g. the Canada zircon in Table 1).

Ni, Co, Pb, Sb. Potential luminescence centers in zircon may be transitional metal ions such as Ni^{2+} and Co^{2+} , which are detected in zircon by ICP-MS (Table 1), EPR (Votyakov et al., 1992) and which are known luminescence centers in phosphors (e.g., Blasse and Grabmaier, 1995). Recently, other centers of broadband luminescence have been identified in minerals using laser-induced time-resolved luminescence, namely d^{10} (Ag^+ , Cu^+) and s^2 (Bi^{3+} , Bi^{2+} , Pb^{2+}) ions (Gaft et al., 2001, 2002). The monovalent ions from the d^{10} group may be excluded given the large difference in ionic charge and the available sites in zircon. Conversely, for several higher valence ions from the d^{10} group, isomorphic substitution in zircon structure is possible in principle, e.g., Zn^{2+} (0.74 Å), Sb^{5+} (0.62 Å) and Te^{6+} (0.56 Å) for Zr^{4+} , and Ga^{3+} (0.61 Å in tetrahedral coordination and 0.76 Å in octahedral) (www.webelements) instead of Si^{4+} and Zr^{4+} . Synthetic zircons artificially activated by several such impurities have been investigated (Fig. 5). Broad bands in the blue–green part of the spectrum characterize all studied impurities with short decay times $< 1 \mu\text{s}$. Nevertheless, such bands have not been detected in natural zircons.

Ti, Ta, V, Sc. Complexes of transition metal ions with a formerly empty d shell often show an intense broadband emission with a large Stokes shift. The presence of Ti, Nb, Ta, V, Mo are confirmed by ICP-MS data (Table 1) and by EPR

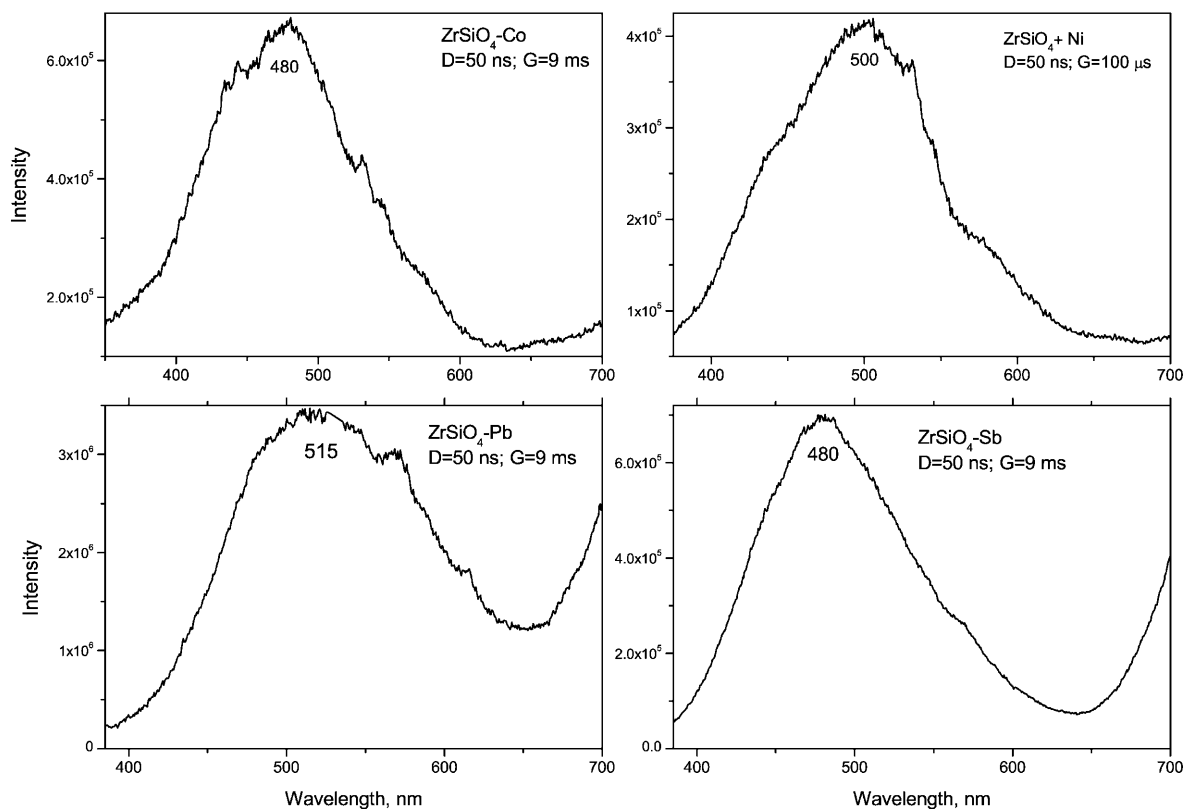


Fig. 5. Laser-induced time-resolved luminescence spectra of ZrSiO_4 activated by Co, Ni, Pb and Sb

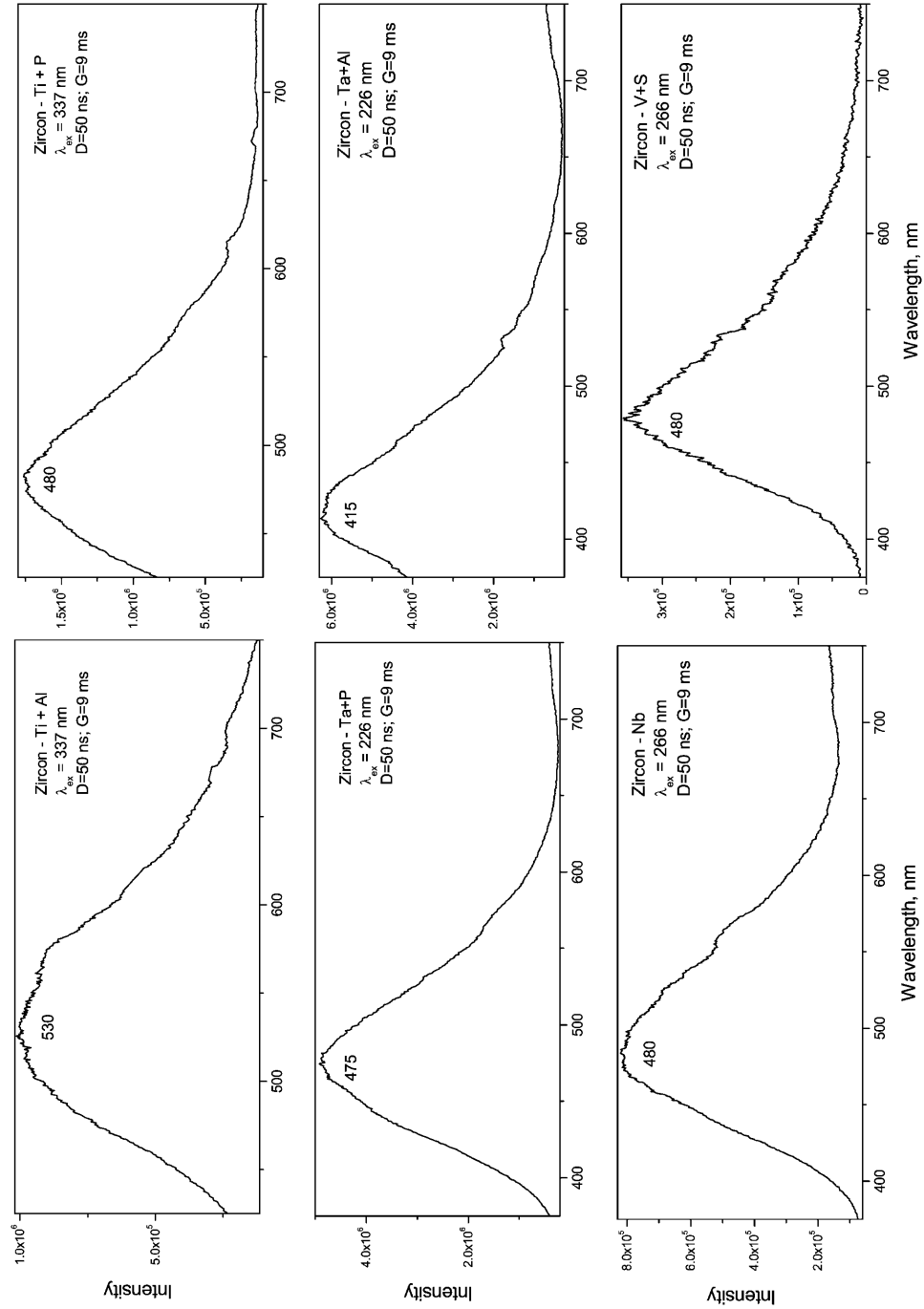


Fig. 6. Laser-induced time-resolved luminescence spectra of $ZrSiO_4$ activated by Ti, Ta, Nb and V

(Votyakov et al., 1992). Synthetic zircons artificially doped by such impurities have been investigated (Fig. 6). Luminescence often depends strongly on the nature of the co-activator, e.g., for Ti and Ta. Nevertheless, as in the previous case, broad bands in the violet–green part of the spectrum characterize all impurities studied with short decay times $< 1 \mu\text{s}$. Such bands have not been detected in natural zircons.

Conclusions

Broadband luminescence of natural zircon in the yellow–orange part of the spectrum is very complicated and controversial. As an additional attempt to clarify the problem, we used laser-induced time-resolved luminescence spectroscopy. The main results may be summarized as follows. The famous yellow band peaking at 575 nm with decay time of 30–35 μs is connected with intrinsic radiation induced luminescence centers. Two luminescence bands have been found, previously hidden under much stronger yellow emission and not detected by steady-state luminescence spectroscopy. They have much longer decay times compared to yellow emission and may be detected only after delay time of $\sim 100 \mu\text{s}$. Those bands peaking at 480 and 515 nm are not detected in pure artificial ZrSiO_4 as before and after different kinds of irradiations and evidently connected with impurities. To identify the exact nature of those impurities, ZrSiO_4 artificially activated by potential activators, such as Mn, Fe, Cr, Ti, Co, Ni, Pb, Sb, have been studied. Nevertheless, the bands similar to those detected in natural zircon are not found and the nature of the corresponding luminescence centers needs further investigation.

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References

- Blasse G, Grabmaier B (1995) Luminescent materials. Springer, Berlin Heidelberg New York, 233 pp
- Gaft M (1992) Application of thermal treatment of zircon for the interpretation of luminescence centers. *J Therm Anal* 40: 67–78
- Gaft M, Rogozin A, Rassulov V, Zukova V (1987) Composite character of yellow photoluminescence of zircon. *Mineral J* 9/6: 63–67 (in Russian)
- Gaft M, Panczer G, Reisfeld R, Shinno I (2000a) Laser-induced luminescence of rare-earth elements in natural zircon. *J Alloys and Compounds* 300–301: 267–274
- Gaft M, Boulon G, Panczer G, Guyot Y, Reisfeld R, Votyakov S, Bulka G (2000b) Unexpected luminescence of Cr^{5+} and Cr^{3+} ions in ZrSiO_4 zircon crystals. *J Luminesc* 87–88: 1118–1121
- Gaft M, Reisfeld R, Panczer G, Saraidarov T, Erlich S (2001) The luminescence of Bi, Ag and Cu in natural and synthetic barite BaSO_4 . *Opt Mat* 16: 279–290
- Gaft M, Siegel H, Panczer G, Reisfeld R (2002) Laser-induced time-resolved luminescence spectroscopy of Pb^{2+} in minerals. *Eur J Mineral* (in press)

- Gorobets B, Rogozin A* (2001) Luminescence spectra of minerals (reference book). VIMS, Moscow, 312 pp (in Russian)
- Hayashi M, Shinno I, Taguchi S, Sugihara S* (1990) ESR signals of zircon irradiated with thermal neutrons and gamma-rays. *J Min Pet Econ Geol* 85: 27–33
- Kempe U, Torsten G, Nasdala L, Wolf D* (2000) Relevance of cathodoluminescence for the interpretation of U–Pb zircon ages, with an example of an application to a study of zircons from Saxonian granulite complex, Germany. In: *Pagel M, Barbin V, Ohnenstetter D* (eds) Cathodoluminescence in geosciences. Springer, Berlin Heidelberg New York Tokyo, pp 425–457
- Krasnobayev A, Votyakov S, Krohalev V* (1988) Spectroscopy of zircons. Nauka, Leningrad, 148 pp (in Russian)
- Shinno I* (1986) Three types of photo-luminescence in natural zircon. *J Jpn Assoc Miner Pet Econ Geol* 81: 433–445
- Shinno I* (1987) Color and photo-luminescence of rare-earth element doped zircon. *Mineral J* 13/5: 239–253
- Taraschan A* (1978) Luminescence of minerals. Naukova Dumka, Kiev, 296 pp (in Russian)
- Votyakov S, Krasnobaev A, Krohalev V* (1993) The problems of applied spectroscopy of minerals. Nauka, Ekaterinburg, 233 pp (in Russian)
- www.webelements.com/webelements/properties/text/definitions/ionic-radius.html

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