

APPLICATION OF THERMAL TREATMENT OF ZIRCON FOR THE INTERPRETATION OF LUMINESCENCE CENTERS

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The photoluminescence (PL) of zircon is characterized by a broad structureless spectral band down to 4.6 K, which does not enable correct interpretation of the nature of the luminescence centres (LC). By applying step-like thermal treatment, a radiation treatment and time-resolved spectroscopy, seven pure bands were separated and their individual spectral-kinetic properties were determined.

The yellow PL is connected with three LC:

1. Intrinsic defects of the $(\text{SiO}_m)^n$ type, which are generated by radioactive decay of U and Th;
2. Impurity defects $(\text{MeO}_m)^n$ (Me – Mo, V) associated with charge compensators, probably the Fe^{3+} and Ti^{3+} (clusters of these LC generate a yellow-orange shoulder);
3. Impurity defects $(\text{UO}_2)^{2+}$.

The blue PL is connected with impurity defects $(\text{TiO}_m)^n$.

The red PL is connected with impurities Fe^{3+} and Ti^{3+} .

These LC are characterized by a different thermal stability and response to ionizing irradiation. This work allows us to propose some practical applications in the fields of dating, dosimetry and genetical mineralogy.

Keywords: luminescence centers, zircon

Introduction

The luminescence of zircon is characterized by a broad structureless spectral band down to 4.6 K, which does not enable correct interpretation of the nature of the luminescent centers (LC). Despite many investigations of the zircon luminescence, there is still no unanimous opinion about its nature [3, 5, 7]. Only recently, publications appeared which claim that broad bands are connected not with one LC but with many LC which

have very similar spectral properties [3, 4, 5]. For this reason, spectroscopic methods alone are not enough for the separation of the broad spectra into individual bands. It is known, however, that thermal treatment has great influence on the luminescence of zircon, and may change its spectra, due to the different thermal stability of the various LC. In this work, we made an attempt to investigate the luminescence of zircon by applying several methods: step-like thermal treatment, radiation treatment and time-resolved spectroscopy (TRS). In the TRS technique, the luminescence spectra are recorded during a very short time at a fixed moment after a laser pulse. These spectra may be totally different from the integrated spectra. After a relatively long time, LC with short decay time will be practically quenched, while in the short time spectrum, contributions from the LC with long decay times will be very small. By these methods, we managed to identify individual luminescence bands and interpret them.

Experimental methods

Time-resolved spectroscopy (TRS) of luminescence was done in the spectral region from 200 to 800 nm, for a time interval from 20 ns to 40 ms and under temperatures from 4.6 to 300 K. The excitation was done by excimer and dye lasers or by an X-ray source. The thermal treatment was carried out in air, in the temperature interval of 380 to 1250 K, in steps of about 50 K. The sample was held for one hour at each temperature and then cooled down to room temperature in the oven. More detailed information can be found in [4].

Results

1. The influence of thermal treatments on the photoluminescence spectra

Photoluminescence spectra (PL) and excitation spectra (ES) of typical zircon samples are presented in Fig. 1. The ES are practically the same under scanning along PL bands and at different temperatures. The decay of the luminescence with time is very complex and is characterized by several components, the relative contributions of which are different on various spectral ranges.

Thermal annealing at temperatures above 800 or 900 K caused spectral changes. A shoulder in the orange region of the spectrum disappears. By TRS one could obtain this band in pure form in some samples (Fig. 2a). In order to check the hypothesis that this band is connected with an individual LC, a large collection of zircon samples of different genesis, was investigated. Some samples showed weak luminescence at 300 K, and bright orange luminescence below 77 K. The decay of this band was found to be exponential, with a decay time of approximately 4–5 mcsec.

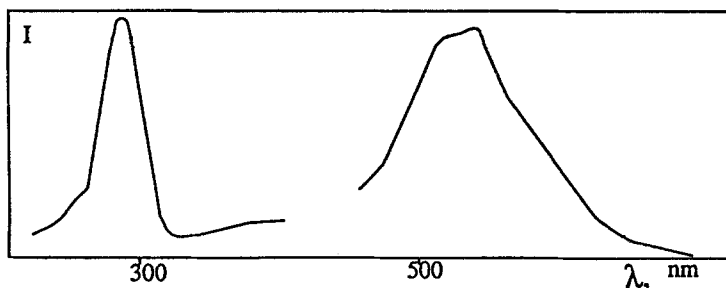


Fig. 1 Photoluminescence spectra (right) of zircon at 300 K (1) and 77 K (2). Excitation spectra (left side) are practically the same under scanning along PL bands and at different temperatures. Excitation source – dye laser

After heating the sample above 900 K, TRS shows that there are at least two bands of yellow PL with practically identical spectral properties, but different decay times.

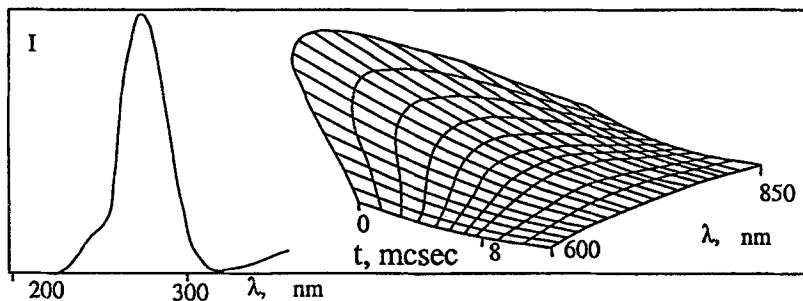


Fig. 2a Photoluminescence (right) and excitation (left) spectra of different zircons: a – Orange band with decay times of 4–5 mcsec and annealing temperatures of 800–900 K

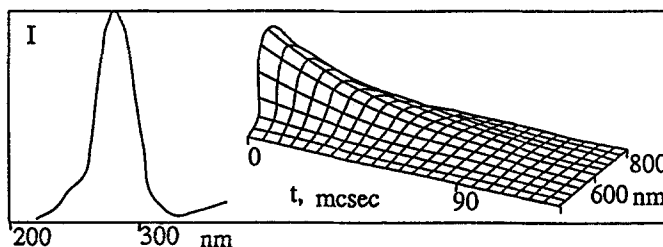


Fig. 2b Photoluminescence (right) and excitation (left) spectra of different zircons: b – Yellow band with decay times of 30–35 mcsec and annealing temperatures of

After heating the sample to temperatures near 1000 K, the component with the longer decay time was missing, and only the one with shorter decay time remained. This evidently means that these components are connected with two different luminescence centres, rather than with two transitions in the same centre. By investigating hundreds

of zircon samples, it was found that there are two groups of zircons with yellow PL. The large group is dominated by a less thermostable band, the decay time of which is approximately 30–35 msec (Fig. 2b) and the smaller one – by a band with a greater thermostability and decay times of 6–10 msec (Fig. 2c). The two bands have different excitation efficiencies given by a recombination mechanism: the first group can not be excited by X-rays while the second is excited quite effectively.

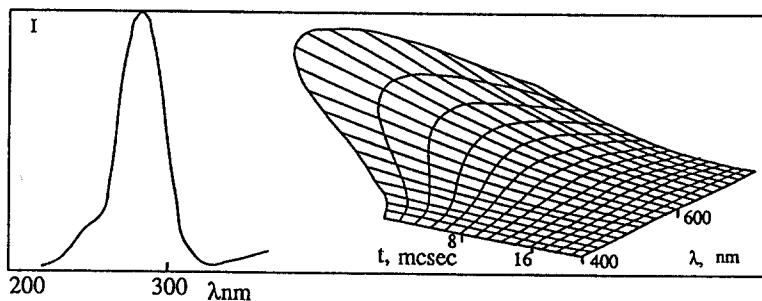


Fig. 2c Photoluminescence (right) and excitation (left) spectra of different zircons: c – Yellow band with decay times of 6–10 msec and annealing temperatures of

After heating the sample above 1150 K, the yellow PL is totally absent in some samples and is persistent in others. Analysis of the spectral and kinetic parameters of this PL gives results which are totally different from those described above (Fig. 2d). The ES maximum moves in the direction of the long waves, and the half-width of the band becomes much smaller. The decay time is 7–8 msec and the intensity below 77 K is larger, by an order of magnitude, than that at 300 K. As the temperature of the thermal treatment rises up to 1250 K, the intensity of this band increases, and after that it decreases sharply.

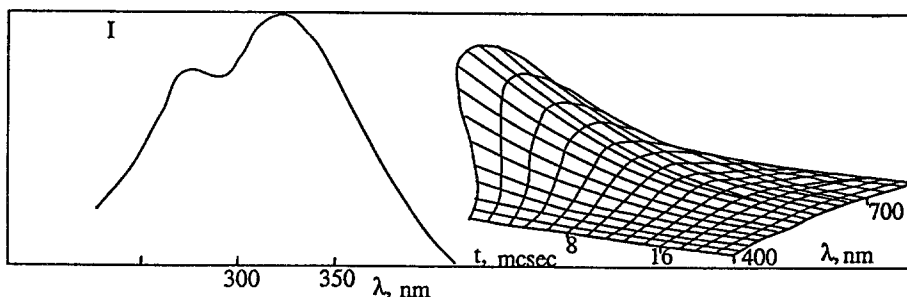


Fig. 2d Photoluminescence (right) and excitation (left) spectra of different zircons: d – Yellow band with decay times of 7–8 msec and annealing temperatures of

Above 1300 K, zircon is characterized by blue and red PL bands. The structure of the red band was found to be practically the same in all the samples. This band consists of two components with different decay times (2 ms and 3–5 msec) (Fig. 2e, f). The in-

interesting feature of this red PL is a drastic decrease of intensity at 77 K, compared to the intensity at 300 K. The intensity of the red PL does not increase with the rising temperature of the thermal treatment, but it is better detected when the centres of the yellow PL are thermally annihilated. The intensity of the blue PL was found to increase at higher temperatures of the thermal treatment. It is characterized by a very short decay time. This band is very effectively excited by the recombination process.

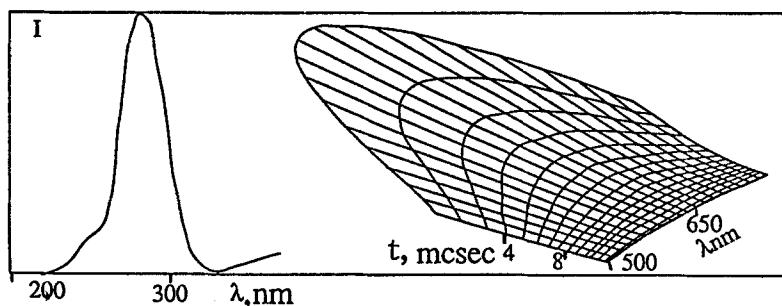


Fig. 2e Photoluminescence (right) and excitation (left) spectra of different zircons: e – Red band with decay time of 2 ms and annealing temperature of above 1350 K

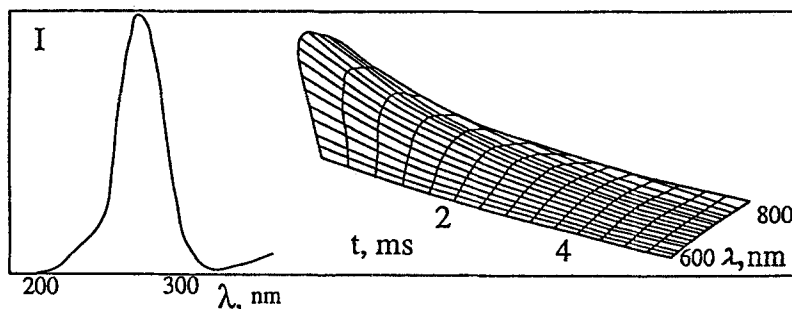


Fig. 2f Photoluminescence (right) and excitation (left) spectra of different zircons: f – Red band with decay time of 3–5 mcsec and annealing temperature of above 1350 K

2. The influence of radiation treatment on the PL spectra after heating

After thermal treatment of the samples at 1300, attempts were made to restore the LC. As in previous investigations [3, 5], irradiations with high doses of X- and gamma-rays did not restore PL. Irradiation by neutrons, or alpha particles, only restored the component with the decay times of 30–35 mcsec in the yellow PL. At the same time, the blue PL reduces its intensity (Fig. 3a).

After irradiation with neutrons and alpha particles, the original unheated zircons showed reduction of the blue and red components and an increase of the yellow and orange ones (Fig. 3b).

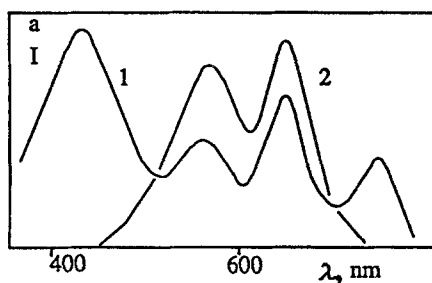


Fig. 3a Photoluminescence spectra of zircons as influenced by thermal and irradiation treatments: a – natural zircon (1) and after alpha irradiation (2)

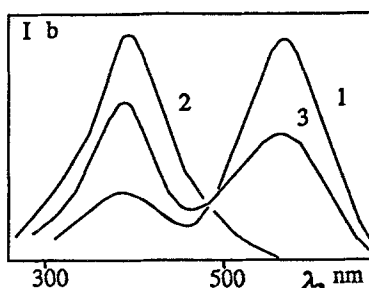


Fig. 3b Photoluminescence spectra of zircons as influenced by thermal and irradiation treatments: b – natural zircon (1), after thermal treatment at 975 K (2) and after thermal treatment at 975 K plus alpha irradiation (3)

In the synthesized nonluminescent analogies of nominally pure zircon, intensive yellow PL appeared after neutron and alpha irradiation with decay time of approximately 35 msec, which is practically the same as in Fig. 2b. Activation by different impurities leads to small changes in PL spectra, but almost always diminishes the intensity.

Discussion

By using thermal treatments in connection with TRS we have, for the first time, an opportunity to separate in pure form, luminescence bands associated with individual LC. This allows us to perform more correct interpretation of their nature, and this is attempted below.

Bands of yellow PL

The nature of this PL in zircon is extremely controversial. There were extensive investigations of its origin, and some authors maintain that it is intrinsic [5]. Others

ascribe it to impurities [3, 7]. It seems that the results of this work may settle this controversy.

The most common band in zircons has its maximum at 570 nm, and has a decay time of 30–35 msec. It is represented in Fig. 2b. Since it can be induced in synthetic, nominally pure samples, by neutron and alpha irradiation, one can deduce that the LC is an intrinsic one. In natural samples, the source of irradiation may be connected with the radioactive decay of U and Th impurities, which are always present in natural zircon. It appears that these LC can be ascribed to lattice defects of the (SiO_m) type, which are induced in zircon by neutron irradiation and were detected by the ESR method [5, 6].

The band with the maximum at 560 nm and decay times of 6–10 msec (Fig. 2c) appears less often. This band could not be induced by irradiations, and is absent in nominally pure synthetic samples. Thus one can conclude that it is associated with an impurity. These LC can be attributed to metal-oxygen complexes (MeO_n) with full electron shells (where the Me are Mo, V) with a nearby charge compensator [3]. In this model the band of orange PL may be ascribed to aggregates of metal-oxygen complexes.

The luminescence band with the maximum at 550 nm and decay times of 7–8 msec (Fig. 2d) can be detected only after heating the sample to a high temperature (1150 K). The spectral properties of this PL indicate that there is a connection with $(\text{UO}_2)^{2+}$, which in many cases is characterized by a narrow band with no vibrational structure. A similar band was discovered in synthetic zircon, activated with U [7]. The presence of optically active U ions is also confirmed by reabsorption and optical absorbance spectra [3].

Bands of red PL

These bands are very rare in natural samples and a thermal treatment at a higher temperature is needed to reveal them. Two kinetic components which differ in their decay characteristics are present at different intensities in some samples. Thus one can conclude that they are connected with different LC rather than with two transitions in one LC. The first component which has a very long decay time is apparently associated with Fe^{3+} in tetrahedral coordination. This centre is characterized by red luminescence and its decay time is in the milliseconds range [6]. The second component may be related to Ti^{3+} which has similar spectral-kinetic properties [3] and is very often detected in zircons by the ESP method [6].

Sharp decrease of the red PL intensity at low temperature is evidence of excitation by a migration mechanism. Since the excitation spectra of yellow and red bands are practically the same (Fig. 2b, c, e), it is possible that at 300 K, only direct excitation of the yellow band takes place, while the red luminescence occurs as a result of the transfer of excitation energy. At 77 K this process of migration becomes ineffective and the red PL disappears. This model is in agreement with known facts about the migration of excitation energy between complexes of metals with full electron shells and transition metals with forbidden (d–d) transitions [1].

As an alternative model, the participation of Sm^{2+} in the red PL may be proposed because this LC has similar spectral characteristics and is often quenched at a low temperature [6]. Ions of Sm^{3+} are identified in zircons by their characteristic PL [5, 7] and the presence of radiation sources makes transformation $\text{Sm}^{3+} \rightarrow \text{Sm}^{2+}$ quite possible.

The band of blue PL

This band is relatively rare in the PL spectra despite the fact that under X-ray excitation it often dominates the spectra. However, owing to its very short decay time, this band is clearly detected in TRS. Blue bands under X-rays and optical excitations showed similar spectral characteristics as well as similar behavior under thermal treatments and irradiation. For this reason, they may be connected with the same kind of LC. If this is the case, this band in PL spectra is generated by titan-oxygen complexes, as was established by experiments with X-ray excitation [5]. The impurity origin of this PL is confirmed by the absence of the band in synthetic, nominally pure samples.

Conclusions

By combining thermal treatment with irradiation and STR we managed to separate from the broad PL spectra of zircon seven pure bands and determine their individual spectral-kinetic properties. Our results explain why there were so many contradictions among conclusions of different investigators, about the nature of the PL of zircon. The reason was the overlapping of bands from basically different LC. Analysis of the present results and other published data allow us to propose the following model:

The yellow PL of zircon is connected with three LC:

1. Intrinsic defects of the $(\text{SiO}_m)^n$ type, which are generated in the natural samples by radioactive decay of U and Th impurities;
2. Impurity defects $(\text{MeO}_m)^n$ (Me—Mo, V) associated with charge compensators, probably the ions Fe^{3+} and Ti^{3+} (clusters of this LC generate a shoulder in the yellow-orange region);
3. Impurity defects $(\text{UO}_2)^{2+}$.

The blue PL of zircon is connected with impurity defects of the $(\text{MeO}_m)^n$ type (Me—Ti).

The red PL of zircon is connected with impurity LC which contain Fe^{3+} and Ti^{3+} .

These LC are characterized by a different thermal stability and their response to ionizing irradiation. The results of this work allow us to propose some kind of practical applications of the zircon PL.

1. In a proposed method of laseroluminescent separation of cassiterite ore, zircon often remains in the concentrate due to its similar PL characteristics under laser excitation [4]. But PL of cassiterite is more thermal-stable (up to

1350 K) and after heating the concentrate up to 1250 K, zircon loses its PL and it is possible to do additional cleaning.

2. The presence of the LC with different responses to thermal treatment gives a preliminary estimation of zircon formation temperature based on the presence or absence of LC with different thermal stability.

3. The PL of zircon is used for separating the mineral from kimberlites. It is known that this zircon usually has the highest intensity of PL [5]. After the separation of the PL bands, it was found that zircon from kimberlites are characterized mainly by specifically $(\text{SiO}_m)^n$ LC with relatively low thermal stability, and a relatively long decay time. Now, using three PL parameters (intensity, THS and decay time), there is a very high probability (near 90%) that zircons may be identified from among the kimberlites.

4. The presence in PL spectra of zircon bands due to alpha-particles influence, together with another methods in principle allow us to estimate the age of zircons. It is possible to use a yellow band which increases with irradiation dose, and a blue band which disappears with the dose. This is of special interest because zircon is a potential material for thermoluminescent dating [5].

The same property can be used for incidental dosimetry of alpha particles. This is also of special interest because PL of zircons is not influenced by gamma irradiation.

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The experimental part of this paper was carried out while the author worked at All-Union Institute of mineral resources (Moscow, Russia).

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Zusammenfassung — Die Photolumineszenz (PL) von Zirkon ist durch eine breite, unstrukturierte Spektrenbande bis 4.6 K gekennzeichnet, was keine korrekte Interpretation des Wesens der Lumineszenzzentren (LC) ermöglicht. Durch Anwendung einer schrittweisen Wärmebe-

handlung, einer Bestrahlung und zeitabhängiger Spektroskopie wurden sieben reine Banden erhalten und deren individuelle spektral-kinetischen Eigenschaften bestimmt.

Die gelbe PL steht mit drei LC in Verbindung:

1. innere Defekte vom $(\text{SiO}_m)^n$ -Typ, die durch den radioaktiven Zerfall von U und Th hervorgerufen werden;
2. Verunreinigungsdefekte $(\text{MeO}_m)^n$ (Me - Mo, V) in Verbindung mit Ladungskompensatoren, wahrscheinlich Fe^{3+} und Ti^{3+} (Cluster dieser LC erzeugen eine gelb-orangene Schulter);
3. Verunreinigungsdefekte $(\text{UO}_2)^{2+}$.

Die blaue PL steht in Verbindung mit Verunreinigungseffekten $(\text{TiO}_m)^n$.

Die rote PL steht in Verbindung mit Fe^{3+} und Ti^{3+} Verunreinigungen.

Diese PL sind durch eine verschiedene thermische Stabilität gekennzeichnet und sprechen auf ionisierende Strahlung an. Vorliegende Arbeit erlaubt den Vorschlag einiger praktischer Anwendungen in den Bereichen Altersbestimmung, Dosimetrie und genetische Mineralogie