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APPLICATION OF THERMAL TREATMENT FOR THE INTERPRETATION OF PHOTOLUMINESCENT CENTRES IN MINERALS

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The influence of thermal treatments on photoluminescence spectra of several minerals has been investigated. By applying step-wise heating, new luminescence centres were detected which had been not previously recognized in the corresponding minerals. Luminsecence centres appearing as result of valence changing during oxidizing heating include:

(i) $(UO_2)^{2+}$ as a result of nonluminescent U^{6+} transformation in zircon, barite, francolite and chert;

(ii) Eu^{2+} as a result of nonluminescent Eu^{+} transformation in barite.

Luminescence centres which were most stable under thermal treatment were Fe^{3+} in zircon and Mn^{2+} in barite. Luminescence centres with similar spectral-kinetic properties but with different thermal stability which allowed them to be separated and properly identified were different metal-oxygen complexes $(MeO_n)^{m-}$ in zircon.

Keywords: photoluminescent centres in minerals

Introduction

The photoluminescence (PL) of many minerals is characterized by broad structureless spectral bands down to 4.6 K, which does not enable correct interpretation of the nature of luminescent centres (LC). However, thermal treatment has a great influence on the luminescence spectra, due to the different thermal stability of the different LCs. In addition, certain cations may change valency during heating, with transformation from nonluminescent form to luminescent. Thus, by applying step-wise thermal treatment it is possible to separate the broad spectra into individual bands.

The aim of this paper is to illustrate the possibilities that such an approach opens for several minerals. Interpretation of the nature of LCs is especially emphasized.

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Experimental

Samples

The minerals described in this paper were selected because their PL is greatly influenced by thermal treatment. Samples from the mineral collections of the All Union Institute of Mineral Resource (Moscow) and the Open University of Israel (Tel-Aviv) were used.

Methods

Physical interpretation of the nature of monomineral-fraction PL was accomplished in an experimental complex described elsewhere [1, 2]. A tunable laser (275–400 nm) was used for excitation. Spectral-kinetic investigation was carried out in the 300–900 nm spectral region fora time between 30 nsec and 40 msec and at temperatures from 300–77 K.

Thermal treatment was carried out in air or in a vacuum, between 380 and 1250 K, and in steps of about 50 K. The sample was held for one hour at each temperature and then left to cool to room temperature.

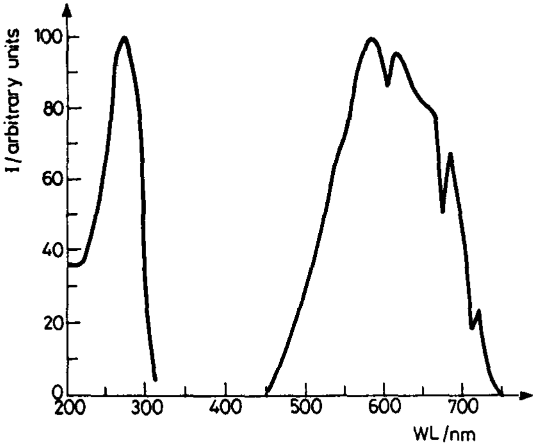

Fig. 1 Photoluminescence spectra (right) of zircon at 77 K. Excitation spectra (left) are practically the same on scanning along PL bands

Results

Zircon, $ZrSiO_4$

PL and excitation spectra of typical zircon samples are presented in Fig. 1. The excitation spectra are almost identical under scanning along PL bands and at different temperatures. Decay of the luminescence with time is characterized by several components. On the longwave part of this band the re-absorption structure often appears (Fig. 1).

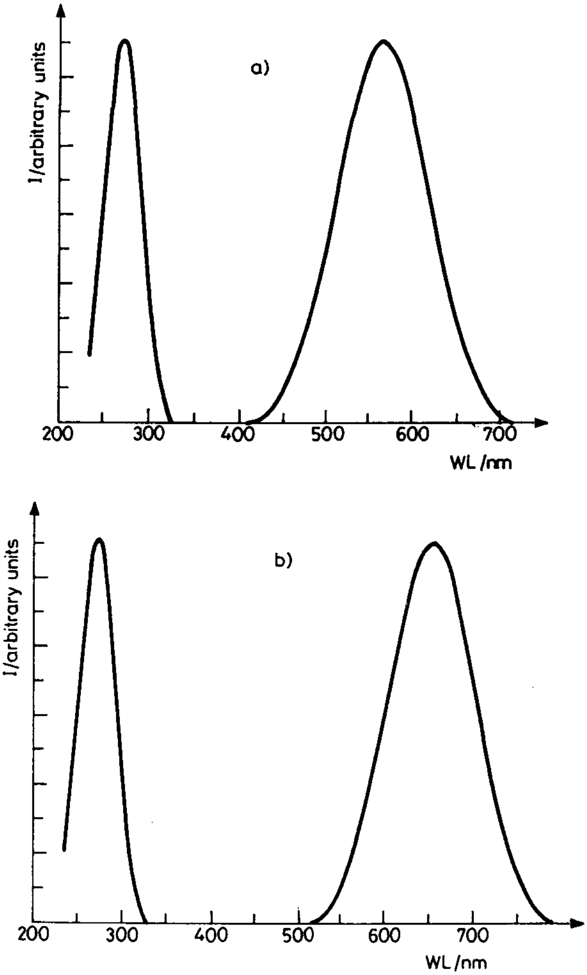

Fig. 2 **a, b** Photoluminescence spectra (right) and excitation spectra (left) of separated bands with different thermal stability: (*a*) yellow containing two components with different decay times (0.004–0.005 and 0.03–0.035 msec) and annealing temperatures of (1000 and 1100 K); (*b*) orange with decay time of 0.005–0.007 msec and annealing temperatures of 900 K;

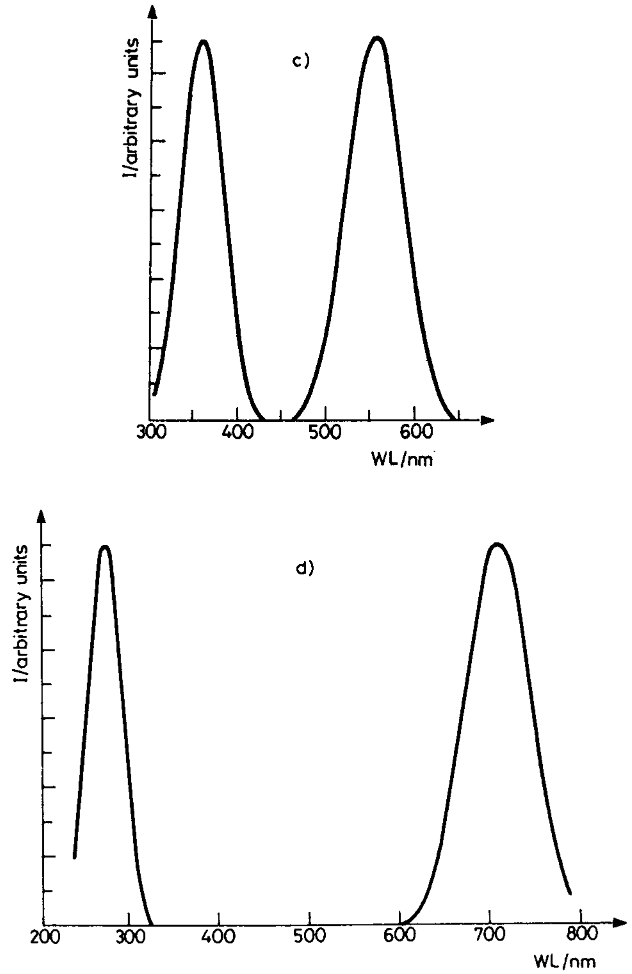

Fig. 2 c, d Photoluminescence spectra (right) and excitation spectra (left) of separated bands with different thermal stability: (*c*) yellow with decay times of 0.007–0.008 msec and annealing temperatures of 1200–1250 K; (*d*) red containing two components with different decay (2 and 0.003–0.005 msec) and annealing temperature above 1350 K

After heating the following observations can be made.

(1) At 900 K a shoulder in the orange region of the spectrum disappears. In the remaining yellow PL (Fig. 2a) two main decay components became dominant – at 0.030–0.035 msec and 0.06–0.010 msec. Investigation of the orange shoulder

revealed that extremely rarely zircon showed a weak PL at 300 K, and a bright orange one at 77 K (Fig. 2b) with a decay time of 0.05 msec.

(2) At 1000K the component with the longer decay time was not present, and only the one with the shorter decay time remained. The two bands have different excitation efficiencies under a recombination mechanism: the first group can not be excited by X-rays while the second is excited quite effectively.

(3) At 1150 K a new type of yellow PL appears in some samples (Fig. 2c), with a decay time of 0.07– 0.08 msec. As the temperature of the thermal treatment approached 1250 K, this band intensity increased but then decreased sharply after this temperature. A similar thermal behavior accompanied the reabsorption.

(4) At 1300 K zircon is characterized by red PL bands (Fig. 2d) with two main decay time components (2 ms and 0.03– 0.05 msec). This PL is characterized by a drastic decrease of intensity at 77 K, compared to its intensity at 300 K.

Barite $BaSO_4$

PL spectra of barite at 300 and 77 K consist mainly of two broad structureless bands (Fig. 3) with complex decay.

After heating at 900 K a new PL appeared. Two types of green LCs were identified with different excitation, vibrational structures (Fig. 4a) and corresponding decay times of 0.35 and 0.25 msec.

In addition, an intesive UV band (Fig. 4b) with a decay time of 0.008 msec, a yellow band (Fig. 4c) with a decay time of 0.45 msec, and an orange band (Fig. 4d) with a decay time of 0.5 ms also appeared.

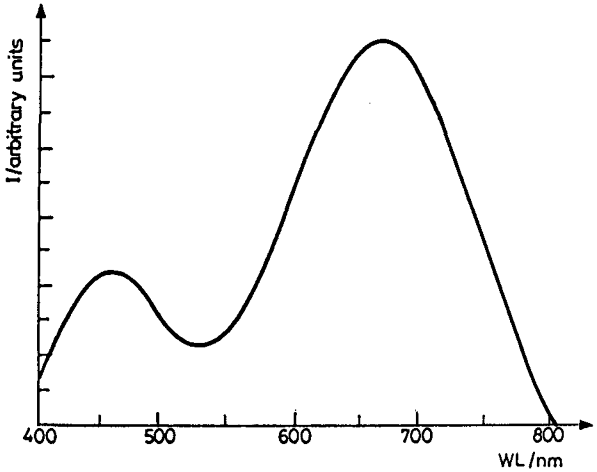

Fig. 3 Photoluminescence spectra of barite at 77 K

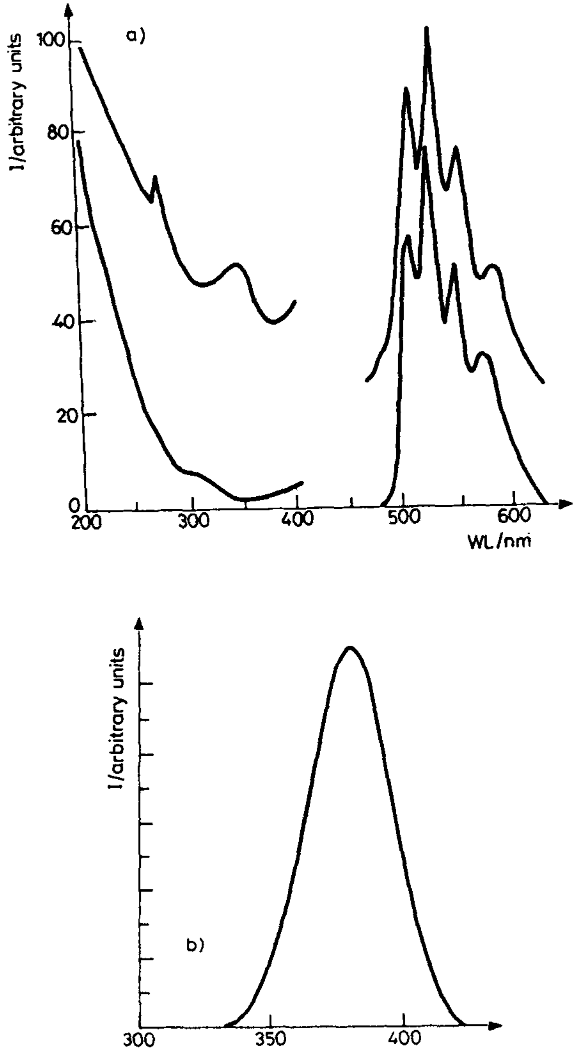

Fig. 4 Photoluminescence spectra of barite after thermal treatment: (*a*) green of two types with decay times 0.35 and 0.25 msec; (*b*) ultraviolet with decay time 0.008 msec;

Francolite $Ca_5(PO_4CO_3)_3F$

PL spectra of francolite consist of several broad bands in UV, violet and yellow ranges (Fig. 5). They are characterized by a complex decay, but in UV the component with 40 ns is dominant, while in violet and yellow the main components are 800 nsec and 1200 nsec.

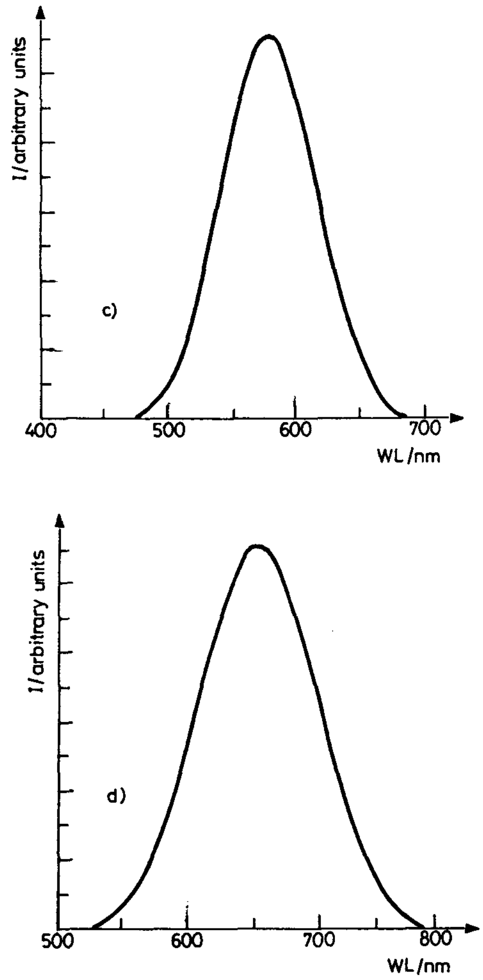

Fig. 4 Photoluminescence spectra of barite after thermal treatment: (*c*) yellow with decay time 0.50 msec; (*d*) red with decay time 0.45 msec

After heating at temperatures above 1100 K the original PL disappeared and a bright green one with characteristic vibrational structure (Fig. 6) and decay time of 0.25 msec appeared.

Chert

Typical PL spectra of cherts even at 300 K exhibit green luminescence with typical series of bands (Fig. 7). Green PL appears only as a result of short-wave excitation, while under long UV excitation yellow PL is observed in some cherts, which is without structure even at 77 K (Fig. 7a).

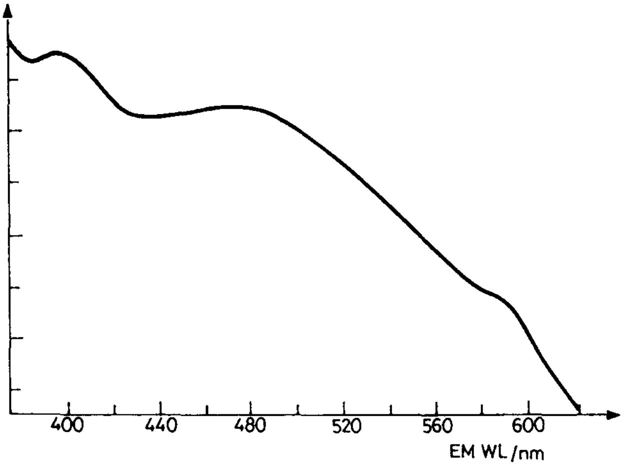

Fig. 5 Photoluminescence spectrum of francolite at 77 K

After heating on air at 1100– 1200 K the yellow luminescence disappeared and a green one with typical structure is seen (Fig. 8).

Discussion

Luminescence centres appearing as result of valence changing

$(UO_2)^{2+}$

The excitation and emission spectra of the structural PL in the green and yellow parts of the spectrum, together with decay time, allows its association with UO_2^{2+} emission from the lowest electronically excited level to excited vibrational levels of the ground state [3– 5]. Different types of uranyl PL most probably indicate several origins. This kind of luminescence has been observed in zircon, barite, francolite, and chert (Figs 2c, 4a, 6, 8). The more intensive luminescence after heating may be connected with oxidation of uranium from 4^+ to 6^+ with transformation of nonluminescent phases to luminescent. In the case of zircon this model is confirmed by the disappearance of reabsorption connected with U^{4+} impurity.

TR^{2+} and TR^{3+}

The marrow UV luminescence band in barite (Fig. 4b), in keeping with its spectral-kinetic properties, is associated with a $6p_{7/2}-8s_{7/2}$ transition in Eu^{2+} [1, 5]. Because this PL appears after oxidizing heating, it may be connected with indirect isomorphic substitution, when initially Eu enters the barite lattice in the form of Eu^{+}, which at 600°C is oxidized to Eu^{2+}. A different crystal field is the reason for the difference is spectral parameter compared with known LC Eu^{2+}, which is formed as result of direct isomorphic substitution.

The nature of the red band (Fig. 4d) appearing in barite ofter heating is unclear and several interpretations are possible. It is known that similar PL is connected with the Eu^{2+} – Eu^{3+} pair, where Eu^{3+} is the sensitizer. To check this, synthesis Eu^{2+}-substituted $BaSO_4$ was heated and red luminescence indeed appeared with parameters similar to the natural samples. However, this PL is similar to synthesis Ag-substituted $BaSO_4$ luminescence [1] and may also be connected with inter-configuration transitions $d^{10}-d^{9}p$ in the Ag^{+} which replaces the Ba^{2+}.

Luminescence centres most stable under thermal treatment

Fe^{3+} and Mn^{2+}

Red bands in zircon (Fig. 2d) are very rare and may be detected only after thermal treatment at a higher temperature when other bands have disappeared. According to spectral-kinetic properties, and as confirmed by the investigation of synthetic $ZrSiO_4$ activated by Fe^{3+}, the component with long decay time is associated with Fe^{3+} in tetrahedral coordination. The nature of the second component is not clear at present.

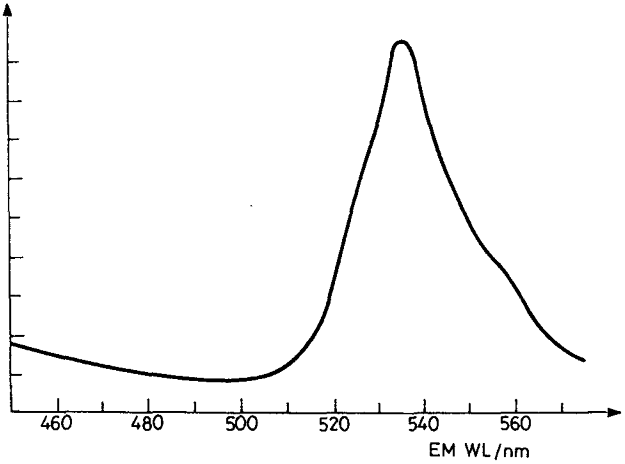

Fig. 6 Photoluminescence spectrum of francolite after heat treatment

Spectral properties of yellow PL, which appeared in barite as a result of heating (Fig. 4c), are similar to those of synthesis Mn-substituted $BaSO_4$ [1] and may be connected with the ${}^4T_1 - {}^6A_1$ transition in Mn^{2+} which replaces Ba^{2+}.

Luminescence centres with similar spectral-kinetic properties but different thermal stability

Metal-oxygen complexes $(MeO_n)^{m-}$

The first separated band with the lowest thermal stability (Fig. 2a) can be induced in synthetic, nominally pure samples, by neutron and alpha irradiation, confirm-

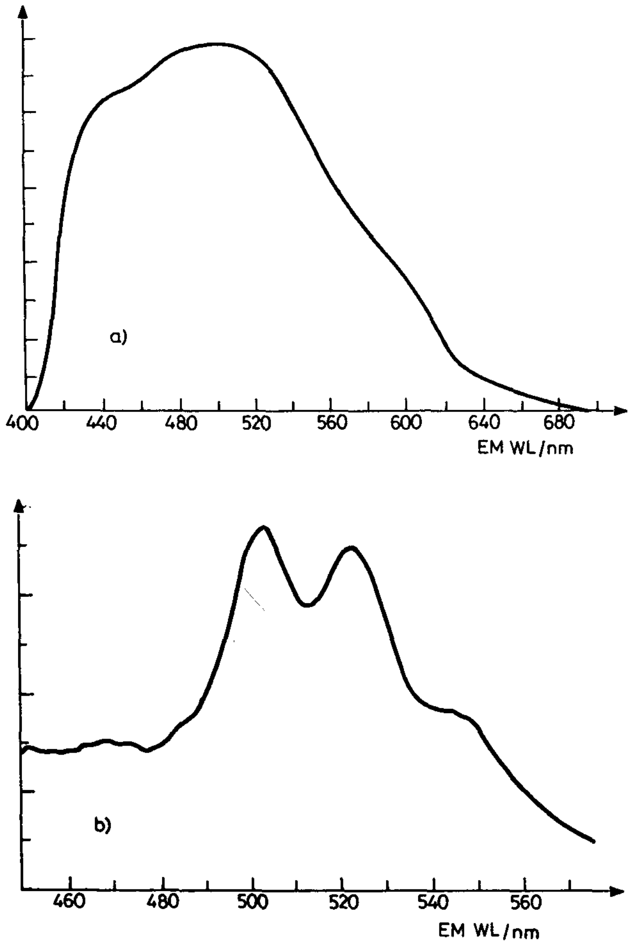

Fig. 7 Photoluminescence spectra of chert: (*a*) green; (*b*) yellow

ing that the LC is intrinsic [3, 6]. 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 LCs can be ascribed to lattice defects of the (SiO_m) type, which are induced in zircon by neutron irradiation. These defects may be detected by electron spin resonance (ESR) and parallel investigation by this method of their formation under neutron irradiation and annihilation as a result of heating shows a good correlation with the corresponding PL band.

The second separated band with higher thermal stability (Fig. 2a) could not be induced by irradiation and is absent in nominally pure synthetic samples. Thus one can conclude that it is associated with an impurity. No correlation of this PL with any ESR centres was found . According to this, LC can be attributed to non-paramagnetic metal-oxygen complexes $(MeO_n)^{m-}$ with full electron shells (where Me are Mo, V) with a nearby charge compensator. In this model the orange PL (Fig. 2b) may be ascribed to aggregates of such complexes.

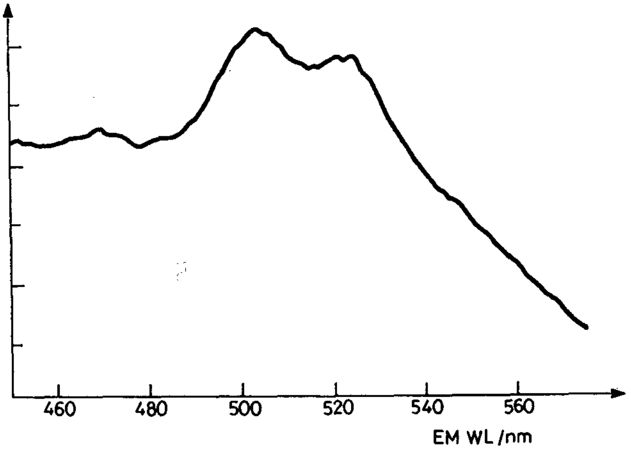

Fig. 8 Photoluminescence spectra of 'yellow' chert after heating

This model allows the nonreversible behaviour of this PL thermal annihilation to be understood. PL disappearance under heating may be connected with valence changing of Me in the complex or with charge compensator vanishing. In the present case Me is already in its highest oxidation state and the second possibility is most likely. This is confirmed by the fact that attempts to obtain such PL in synthesised $ZrSiO_4$ with any one activator were not successful. It is possible, that two co-activators are needed, as in the case of YPO_4, which has a structure similar to that of zircon. Here activation with V^{5+} leads to the appearance of blue PL, but coactivation with V^{5+} and Bi^{3+} changes PL colour to yellow [7].

The exact nature of the charge compensators is unknown, but some speculations are possible. As noted previously, the red PL of Fe^{3+} has the same excitation as yellow PL and is quenched at a temperature 77 K with a increase of yellow PL intensity. It is suggested that sensitization plays an important role in the excitation mechanism. At 77 K, energy migration is more difficult and red PL is quenched. Three migration mechanisms are known [3]: emission–reabsorption, resonance radiationless, and nonresonance radiationless (exchange). Experiments have revealed that excitation of another yellow band, connected with $(UO_2)^{2+}$, does not lead to Fe^{3+} luminescence. For the first two mechanisms of energy migration a necessary condition for transfer is either the closeness of the emission energy of one ion to the absorption energy of the other, or coincidence between energy level pairs of the sensitizer and the activator. Thus these mechanisms have to be effective for all activators with yellow luminescence characterized by similar spectral parameters. Because this is not the case, the exchange mechanism is the most probable one. This mechanism comes into play over very short distances (up to 7–8 Å) and for this reason, a very close association of Fe^{3+} and $(MeO_n)^{m-}$ centres must ixist. Consequently, Fe^{3+} may be a charge compensator in this case. This model is in accordance with known facts of energy migration between $(MeO_n)^{m-}$ complexes and ions with forbidden (*d*-*d*)-transitions with effective luminescence quenching [8].

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Zusammenfassung — Der Einfluß von Hitzebehandlungen auf das Photolumineszenzspektrum verschiedener Minerale wurde untersucht. Durch schrittweises Erhitzen wurden neue Lumineszenzzentren gefunden, welche in natürlichen Mineralen bisher nicht erkannt wurden. Lumineszenzzentren, die im Ergebnis der Valenzänderung bei oxidierendem Erhitzen auftreten, beinhalten
(i) $(UO_2)^{2+}$ als Ergebnis der nichtlumineszenten U^{6+}-Umwandlung in Zirkon, Baryt, Franzolit und Hornstein;
(ii) Eu^{2+} als Ergebnis der nichtlumineszenten Eu^{+}-Umwandlung in Baryt. Die bei Hitzebehandlung stabilsten Lumineszenzzentren waren Fe^{3+} in Zirkon und Mn^{2+} in Baryt. Lumineszenzzentren mit ähnlichen spektral-kinetischen Eigenschaften, aber unterschiedlicher thermischer Stabilität, was es erlaubt, sie zu trennen und entsprechend zu identifizieren, waren verschiedene $(MeO_n)^{m-}$ Metall-Sauerstoff-Komplexe in Zirkon.