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Dedicated to Professor Lisa Heller-Kallai on the occasion of her 65th birthday

LASER-INDUCED LUMINESCENCE OF BARITE AFTER THERMAL TREATMENT

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Abstract

The photoluminescence (PL) of barite is a noncharacteristic property and cannot be used for the investigation of its structure. After thermal treatment of barite at 600°C several luminescent centers were observed, providing information about different impurities. UO_2^{2+} was determined from the vibrational structure and the long decay time of the luminescence band. Two different types of uranyl were detected, thin films of uranyl mineral (most probably, reserfordin) and a solid solution of uranyl ion in barite crystal. Characteristic green luminescence of UO_2^{2+} may be used as indicative feature for the prospecting of uranium deposits and for the sorting of barite ores with the aim of cleaning from harmful U impurities. Eu^{2+} was determined from the spectral position, the half-width and the characteristic decay time of the luminescence band.

Mn^{2+} and Ag^+ were determined by comparing luminescence bands spectral parameters to those of synthesized $BaSO_4$-Mn and $BaSO_4$-Ag. Fe^{3+} or Mn^{4+} were determined from the spectral-kinetic parameters of the luminescence bands.

Keywords: barite, laser-induced luminescence

Introduction

It has been known for a long time that some specimens of barites are fluorescent under UV exposure and emit white, yellow or orange light [2]. In order to understand the nature of this phenomenon, the luminescence spectra of barite were examined via UV lamp, thermal and X-ray excitation [4, 5, 13, 15]. It was discovered that under lamp excitation luminescence of barite is characterized by broad structureless bands down to 77 K, which does not enable correct interpretation of the luminescence centers (LC). Under X-ray excitation intense intrinsic luminescence, which is apparently connected with lattice defects SO_4^{2-}, was observed. The almost total absence of impurity luminescence was explained by the fact that barite usually contains only very small quantities

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of potential luminogens compared, for example, with celestine, anhydrite, or fluorite. It is associated with the relatively big difference between the ionic radii of Ba^{2+} and the usual cationic LC in minerals (TR^{2+}, TR^{3+}, Mn^{2+}) compared with Sr^{2+} and Ca^{2+} [4, 5].

Recently, the spectral-kinetic properties of barite luminescence have been investigated under UV laser excitation. It was discovered that even under this powerful and selective excitation the luminescence spectra are still uncharacteristic. However, the decay time curve contains several components [6]. Usually this indicates the presence of several individual luminescence bands. A very similar situation was encountered in the luminescence of zircon, where only step-like thermal treatment allowed for separation into individual bands and interpretation [8].

Taking these observations into account, we applied thermal and radiation treatments for the barite luminescence investigation. Under this treatment the luminescence appeared in a much more characteristic form, and we were able to detect and identify several previously unknown LC and interpret the mechanism of their formation.

Experimental

The apparatus has been described in detail elsewhere [6]. An N_2 (337 nm) and eximer (222 and 308 nm) lasers were used as excitation sources. Usually, the laser pulse energies are between 40 and 120 mJ. The pulse width ranges between 10 and 15 nsec, and pulse repetition range is typically 50 Hz.

Spectral-kinetic investigation was carried out in the spectral region of 350 to 900 nm, at a time interval between 30 nsec and 40 msec and at temperatures of 300 to 77 K. The luminescence was collected and passed through a monochromator with a dispersion of 1 nm/mm. Dichroic filters were used to reduce the scattered laser radiation. The light was detected by a photomultiplier whose output was digitized by an analog-to-digital converter interfaced with a minicomputer. The signals were averaged over a specified number of laser pulses and stored. To obtain the luminescence spectra, the monochromator was stepped by the computer over the wavelengths until the desired spectral range was covered. To obtain the decay curve, signal timing was provided by a pulse generator which triggered the laser and, after a fixed delay time, triggered the computer to start data acquisition. Following signal averaging the process was repeated after the different delay times. The luminescence decay time was obtained from a fit of a single exponential decay to the signal at the fixed wavelength. The optical system and detector were calibrated by means of standard luminofors with known spectral and kinetic parameter. This calibration allowed for corrections for variations in the instrumental response to be made.

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. Irradiation was carried out by the X-ray source.

Results

Spectra of barite laser-induced luminescence (LIL) at 300 K consisted mainly of two broad bands, the more intense one is in the yellow-orange part of the spectra with a maximum at 620 nm and a half-width of 180 nm (Fig. 1a). These were characterized by a complex decay with many components and mainly by the absence of structure down to 77 K.

Some samples showed red luminescence at 300 and 77 K (Fig. 1b) with a maximum at 670 nm, and a half-width of 95 nm. The decay time was 0.45 ms. The luminescence was not excitable by X-rays.

Thermal annealing at temperatures of up to 900 K did not cause spectral changes, but above that temperature drastic alterations took place.

An original yellow-orange band became narrower and its maximum shifted slightly to the shortwave direction. At 77 K samples were characterized by green LIL with vibrational structure (Fig. 2a, 1) and a decay time of 250 msec. The samples with original red LIL after heating were characterized by sites with green, yellow and remaining red LIL. Spectra of the green LIL were the same as earlier (Fig. 2a, 1), but they may be observed even at 300 K. Besides that, at 77 K a new green structured LIL appeared with excitation and emission spectra different from the previous ones (Fig. 2a, 2). The spectrum of yellow luminescence consists of broad band wit a maximum at 575 nm, a half-width of 90 nm, and a decay time of 0.45 msec (Fig. 2b).

On some samples an intensive UV band appeared with a maximum at 380 nm, a half-width of 40 nm, and a decay time of 0.8 msec (Fig. 2c).

On some samples an orange band appeared with maximum at 640 nm, a half-width of 110 nm, and a decay time of 0.5 msec (Fig. 2d).

After X-ray irradiation of heated samples it was established that the LIL spectra had changed.

Together with the UV band, a broad shoulder in a visible region appeared with a resulting change of LIL color from violet to blue (Fig. 2c). The blue band was very unstable and after 20 min of laser irradiation its intensity sharply diminished. Heating of the irradiated samples totally erased the blue band and the original UV reappeared.

After 40 min of X-ray irradiation red LIL, which retained after heat treatment (Fig. 1b), sharply diminished its intensity. The orange band appearing as result of heating (Fig. 2d), did not change under X-ray influence.

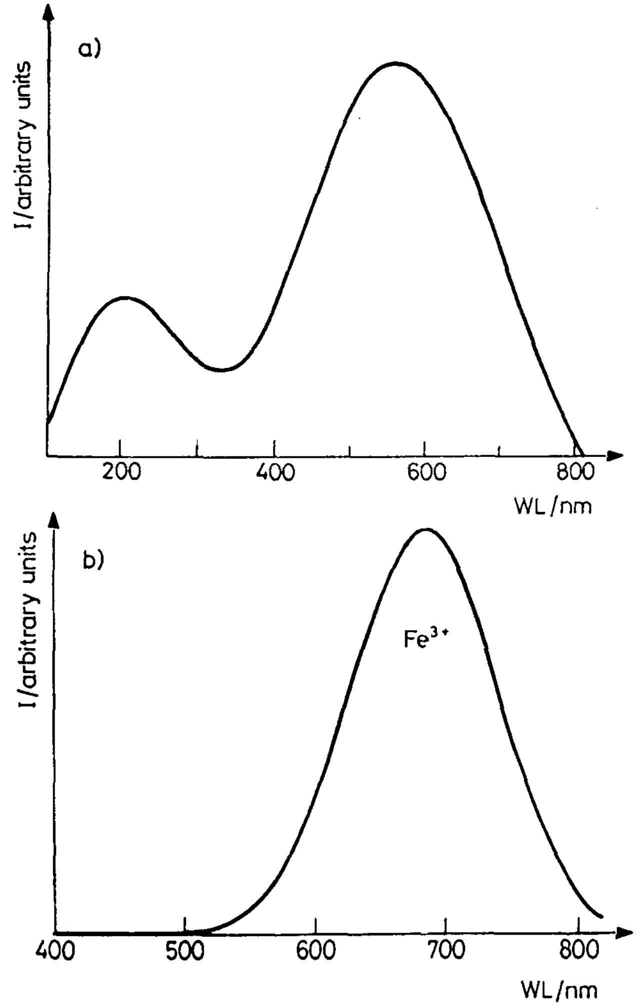

Fig. 1 Different photoluminescence spectra of natural barites (UV laser excitation): a - many centered yellow-orange luminescence; b - red luminescence, supposedly connected with Fe^{3+} or Mn^{4+}

Discussion

Green luminescence

The excitation and emission spectra of the green luminescence, 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, 11, 12, 14, 15]. In the case of barite, two different types of uranyl luminescence (Figs 2a and 2b) most probably indicate its presence in the several forms. Three different models of uranyl ion interrelation with host mineral were proposed earlier [3, 14]:

films of uranyl-containing minerals;

presence in the matrices that are relatively transparent at the excitation and luminescence wavelengths of UO_2^{2+};

physical sorption of uranyl aquacomplexes.

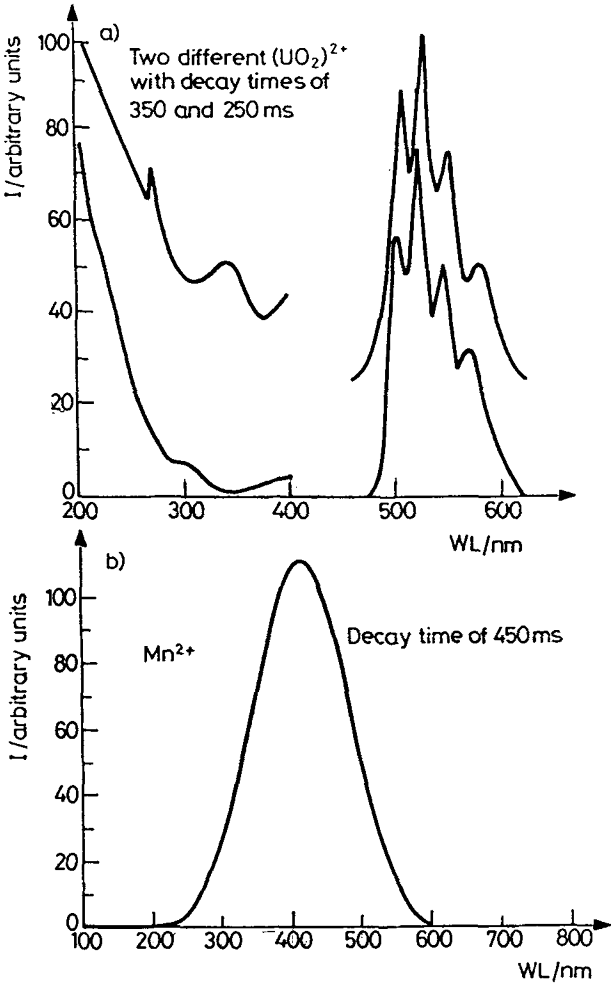

Fig. 2a,b Different photoluminescence spectra of barite after thermal treatment at 600°C (UV laser excitation): a - green luminescence connected with two different $(UO_2)^{2+}$; b - yellow luminescence connected supposedly with Mn^{2+}

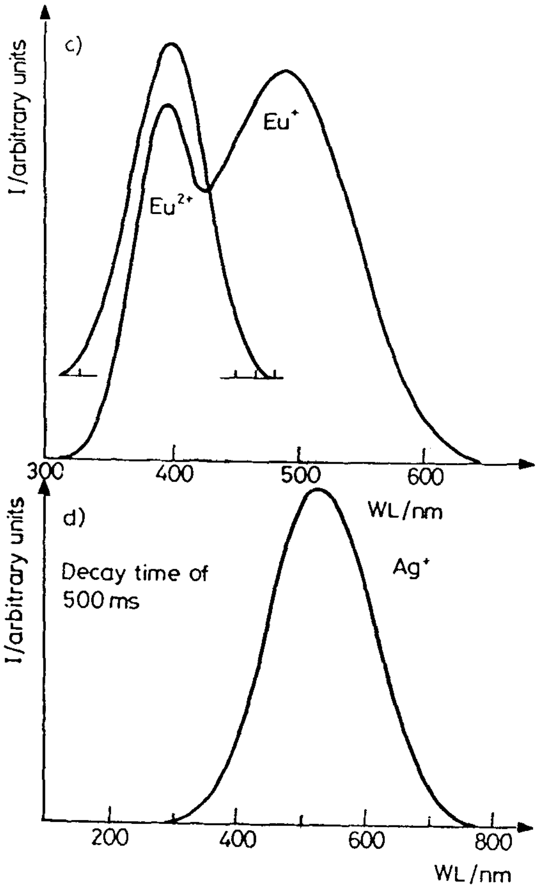

Fig. 2c, d Different photoluminescence spectra of barite after thermal treatment at 600°C (UV laser excitation): c - violet luminescence connected with Eu^{2+} and blue-violet luminescence after X-ray irradiation of the heated barite, where the blue shoulder supposedly connected with Eu^{+}; d - orange luminescence supposedly connected with Ag^{+}

Investigation of the green luminescence excitation spectra demonstrated that the first LC shown in Fig. 2a are excited better in their longwave part, which is characteristic of the films of uranyl mineralization. Comparison with uranyl minerals luminescence demonstrated that the most similar spectral parameters has mineral reserfordin [14]. The shortwave enhancement is more prominent for the second LC shown in the Fig. 2a. This is usually connected with diluted nature of mineralization in the form of uranyl ions in the host mineral lattice [3].

The more intensive luminescence after heating may be connected with oxidation of uranium from 4^{+} to 6^{+} or with transformation of nonluminescent phases to luminescent.

This kind of luminescence has been observed in samples from uranium deposits, but has never been found in barites not connected with uranium mineralization. Thus, the green luminescence of barite after heat treatment at 600°C may serve as an indicator in uranium prospecting. In addition, as in the case of Negev phosphorites [7], luminescent sorting may make it possible to separate lumps with elevated concentrations of U in order to clean the industrial products from this harmful impurity.

Ultraviolet luminescence

Usually narrow luminescence bands in the UV-blue spectral region are connected with $^6P_{7/2}$ – $^8S_{7/2}$ transitions in Eu^{2+} impurity [6, 12, 15–18]. Luminescence of Eu^{2+} is known in many minerals, including barite, where two different forms of this LC presence were established. The first of them is connected with isomorphic substitution of Eu^{2+} instead of Ba^{2+} and the second form is related with Eu^{2+} which was formed after Eu^{3+} – Eu^{2+} transformation as result of ionizing irradiation [5].

Spectral position, half-width and especially decay time of the UV band, discovered in barite (Fig. 2c), are confident characteristics that this luminescence is also connected with Eu^{2+}. Luminescence appearance only after oxidizing heating evidences that it is connected with some kind of transformation which takes place in barite lattice at these conditions. We suppose that the following model is possible. This luminescence is generated by Eu^{2+} which was formed as result of indirect isomorphic substitution, when Eu initially enters the barite lattice in the form of Eu^{+}, which oxidizes to Eu^{2+} at 600°C. The relatively small difference between the Ba^{2+} and the Eu^{+} ionic radii (1.49 and 1.70 Å) makes this substitution principally possible under the conditions of charge compensation. The very high intensity of this luminescence indicates that the greatest part of Eu in such barites enters the lattice as Eu^{+}. The crystal field around this LC is different from that occurring with the direct substitution of Eu^{2+} for Ba^{2+} and is the cause of the different spectral parameters.

Luminescence of Eu^{+} was still not observed in minerals but is well known and studied in synthesized luminofors [9, 10]. This LC usually generates the broad-band luminescence in the blue part of the spectrum. These facts are in accordance with the observed disappearance of UV band of Eu^{2+} under X-ray irradiation with simultaneous appearance of blue band (Fig. 2c). According to our model, this luminescence is connected with Eu^{+} formed as result of irradiation induced Eu^{2+}– Eu^{+} transformation. It is also possible that Eu^{+} takes part in the generation of blue luminescence in the barite (Fig. 1a).

Longwave luminescence

In the yellow-red part of the spectra three LC can be observed. The interpretation of these bands is usually rather difficult because of their relative broadness and the absence of fine structure. Despite this, the combination of spectral-kinetic parameters and thermal behavior makes it possible to come to certain conclusions about their nature.

Spectral properties of the yellow band which appeared after heating (Fig. 2d) are very similar to those of synthesized $BaSO_4$-Mn [5, 13]. According to this, the origin of the luminescence under consideration may be connected with $^4T_1$ – $^6A_1$ transition in the Mn^{2+}, most probably instead of Ba^{2+}. The big difference in the ionic radii of Mn^{2+} (0.87 Å) and Ba^{2+} (1.49 Å) may lead to the lowering of crystal field symmetry and the diminishing of decay time, which in the case of Mn^{2+} is usually at intervals of several ms [5, 12, 15–18]. The appearance of this band only after heating may be connected with the high thermal stability of this LC, which maintains its luminescence intensity.

Spectral properties of the red band which appeared after heating (Fig. 2d) are very similar to those of synthesized $BaSO_4$-Ag [5, 13]. The origin of such luminescence may therefore be connected with inter-configuration transitions d^{10}–d^9p in the Ag^+. The presence of Ag^+ is quite likely in view of the similarities between the Ba^{2+} (1.49 Å) and Ag^+ (1.4 Å) ionic radii.

The broad red bands in minerals are usually connected with either of two LC: $^4T_1$– $^6A_1$ transition in Fe^{3+} (ionic radius 0.64 Å) in tetrahedral coordination, or $^4T_1$–$^4A_2$ transition in Cr^{3+} (ionic radius 0.63 Å) in octahedral coordination [5, 12, 15–18]. The structure of barite is characterized by SO_4 tetrahedrons while Ba is coordinated by twelve oxygens [1] and it is very difficult to find the possible structural positions of these impurities because there are significant differences in ionic radii with Ba^{2+} (ionic radius 1.49 Å), and, similarly, bit charge and radius differences with S^{6+} (ionic radius 0.3 Å). We consider a connection of this luminescence with Fe^{3+} in tetrahedron on the S^{6+} site to be the more likely, especially because it is known that in powellite $CaMoO_4$ and wulphenite $PbMoO_4$, Fe^{3+} occupies the Mo^{6+} site rather then the Ca^{2+} (Pb^{2+}) site [1].

At the same time, another interpretation is also possible. It is known, that the ion Mn^{4+} has a d^3 electronic configuration as Cr^{3+} and is important as an activator in some phosphors, but it does not commonly occur in minerals [18]. We consider a connection of this red band with LC Mn^{4+} to be possible in principal, according to the following reasons:

spectral-kinetic properties are in accordance with $^4T_2$–$^4A_2$ transition;

ionic radius (0.5 Å) and charge of Mn^{4+} are nearer to the corresponding S^{6+} parameters compare with Fe^{3+} and Cr^{3+};

according to ESR ionic impurities of Mn^{5+} and MnO_4^- were discovered in barite in tetrahedral coordination [1].

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Zusammenfassung — Die Fotolumineszenz (PL) von Baryt ist keine charakteristische Eigenschaft und kann nicht zur Untersuchung seiner Struktur eingesetzt werden. Nach einer thermischen Behandlung von Baryt bei 600°C wurden einige Lumineszenzzentren beobachtet, die Informationen über verschiedene Verunreinigungen liefern. Anhand der Schwingungsstruktur und der langen Abklingzeit der Lumineszenzbande wurde UO_2^{2+} bestimmt. Es wurden zwei verschiedene Uranyl-Typen beobachtet: dünne Schichten von Uranylmineralien (wahrscheinlich Reserfordin) und eine feste Lösung von Uranylionen in Barytkristallen. Die charakteristische grüne Lumineszenz von UO_2^{2+} kann als indikative Eigenschaft für die Suche nach Uranlagerstätten verwendet werden und für das Sortieren von Baryterzen durch Reinigung von schädlichen U-Verunreinigungen wurde Eu^{2+} anhand der spektralen Lage, der Halbwertsbreite und der charakteristischen Ausklingzeit der Lumineszenzbande bestimmt.
Mn^{2+} und Ag^+ wurden durch einen Vergleich der Spektralparameter der Lumineszenzbanden mit denen von synthetisiertem $BaSO_4$-Mn und $BaSO_4$-Ag bestimmt. Fe^{3+} und Mn^{4+} wurden anhand der spektralkinetischen Parameter der Lumineszenzbanden ermittelt.