Spectroscopic study of barite from the Kremikovtsi deposit (Bulgaria) with implication for its origin

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Abstract. Different genetic types (endogene and supergene) of barite from the Kremikovtsi deposit (Bulgaria) were studied by Laser-induced time-resolved luminescence (LITRL), Infrared (IR) and Raman spectroscopy. The IR spectra of the endogene barites are quite similar to those reported in the literature and do not show appreciable differences among them. The IR spectra of the supergene barites are almost identical to those of the endogene ones in respect to the positions of the vibrational modes v_1, v_2 and v_4 of SO_4^2, except for a shift of 3 cm^{-1} for the v_3 band. They displayed a presence of additional bands, which are close to the v_3 and v_1 modes of CO_3^{2-} in calcite. The Raman studies support the suggestion that the supergene barite contains traces of calcite.

The modern LITRL technique allowed the detection of several luminescent centers in the endogene barite. Eu^{3+} luminescence was identified for the first time in barite. The different emission spectra at 266 and 532 nm excitations suggest there are at least 2 structural positions for Eu^{3+} in the barite crystal lattice. The luminescent spectra also revealed a rather unusual violet-blue Nd^{3+} emission, which usually occurs in the IR spectral range, as well as emissions of Ce^{3+}, Eu^{2+}, Tb^{3+}, Ag^+, Sn^{2+}(?) and UO_2^{2+}.

The oxidation state of cations isomorphically present in the barite crystal lattice suggests the endogene barite in the Kremikovtsi deposit precipitated from reduced fluids supposedly subjected to cooling (conductive/convective) and oxidation (mixing with seawater).

Key words: barite, UV Time-resolved Luminescence, IR spectroscopy, Raman spectroscopy, Kremikovtsi deposit, Bulgaria.

Апстракт. Различити генетски типови барита (ендогени и супергени) из кремиковачког лежишта у Бугарској проучавани су спектроскопским методима LITRL, IR и Раман. Инфрацрвени спектри ендогених барита слични су спектрима из литературе и не показују међусобне разлике. IR спектри супергених барита су скоро идентични спектрима ендогених барита у погледу положаја вибрационих пикова v_1, v_2 и v_4 SO_4^{2-} осим за помак од 3 cm^{-1} код v_3. Спектри су приказивали присуство додатних трака које су блиске пиковима v_3 и v_1 CO_3^{2-} у калциту. Раманова спектроскопска проучавања иду у прилог наговештаја да супергени барит садржи трагове калцита.

Савремена техника LITRL омогућава откривање неколико луминесцентних центара у ендогеним бариту. По први пут је у бариту утврђена луминесценција Eu^{3+}. Различити емисиони спектри при побуђивању од 266 и 532 nm указују да постоје бар два структурна положаја Eu^{3+} у кристалној решетки барита. Луминесцентни спектри су такође открили необичну љубичасто-плаву емисију Nd^{3+}, која се обично јавља у инфрацрвеном опсегу спектра, као и емисије Ce^{3+}, Eu^{2+}, Tb^{3+}, Ag^+, Sn^{2+}(?) и UO_2^{2+}.

Степен оксидације катјона изоморфно присутних у кристалној решетки барита указује да је ендогени барит у лежишту Кремиковци наталожен из редукованих флуида за које се претпоставља да су били изложени хлађењу (кондуктивно односно конвективно) или оксидацији (мешањем са морском водом).

Кључне речи: барит, ултравиолентна луминисценција, инфрацрвена спектроскопија, Раман спектроскопија, лежиште Кремиковци, Бугарска.

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Introduction

A large share of the known and mined reserves of various metals (Pb, Zn, Cu, Ag, Hg, Sb, less Fe and Mn) are concentrated in carbonate-hosted polymetallic deposits of the sedimentary exhalative (SEDEX) type. A large Phanerozoic deposit of this type, the Kremikovtsi iron(+Mn)-barite-sulphide deposit in Bulgaria, which has been mined for iron, also contains large reserves of barite ore (29 million tons of barite ore and over 60 million tons of $BaSO_4$). Investigations of this deposit have mainly been focused on the iron ores (DAMYANOV, 1998, and the references therein). There are just a few studies on the mineralogy and geochemistry of barite (ATANASSOV & VASSILEVA, 1987; ZLATEV & MLADENOVA, 1997; VASSILEVA et al., 2001; DIMOVA, 2006) and only one of them (ATANASSOV & VASSILEVA, 1987) presents a brief spectroscopic (IR and thermoluminescence) characterization of the Kremikovtsi barite. All these approaches, however, are based on routine conventional techniques (X-ray diffractometry, emission spectroscopy). In order to gain more insight into the barite structure and cation valence with implications for its origin, a set of modern methods (LITRL, IR and Raman spectroscopy) was used. Here, spectroscopic data for barite from this deposit, with emphasis on the results obtained using the laser-induced time-resolved luminescence technique, are reported.

Geological setting

The Kremikovtsi deposit (Fig. 1) lies in the southernmost part of the Kremikovtsi–Vratsa ore district, located in the eastern part of the Western Balkanides, which belong to the northern branch of the global Alpine–Hymalayan collisional orogenic belt on the Balkan Peninsula. The lithology of the region is presented by Paleo-, Meso- and Neozoic sedimentary rocks (Fig. 1). A major tectonic element is the Kremikovtsi thrust. The deposit is hosted in Middle Triassic dolomitic limestones in the western part of the Kremikovtsi thrust sheet. It consists of stratiform and lenticular iron formations and barite orebodies subparallel to the allochton bedding plane and subvertical (pipe-like) bodies of low-grade sulfide mineralization (DAMYANOV, 1998).

Two main genetic types of barite were found in the Kremikovtsi deposit – endogene and supergene (ATANASSOV & VASSILEVA, 1987), and 3 main morphological types of endogene barite bodies were distinguished: veins and lenses, veinlets and nests, impregnations (DIMOVA, 2006). Supergene barite occurs as colloform
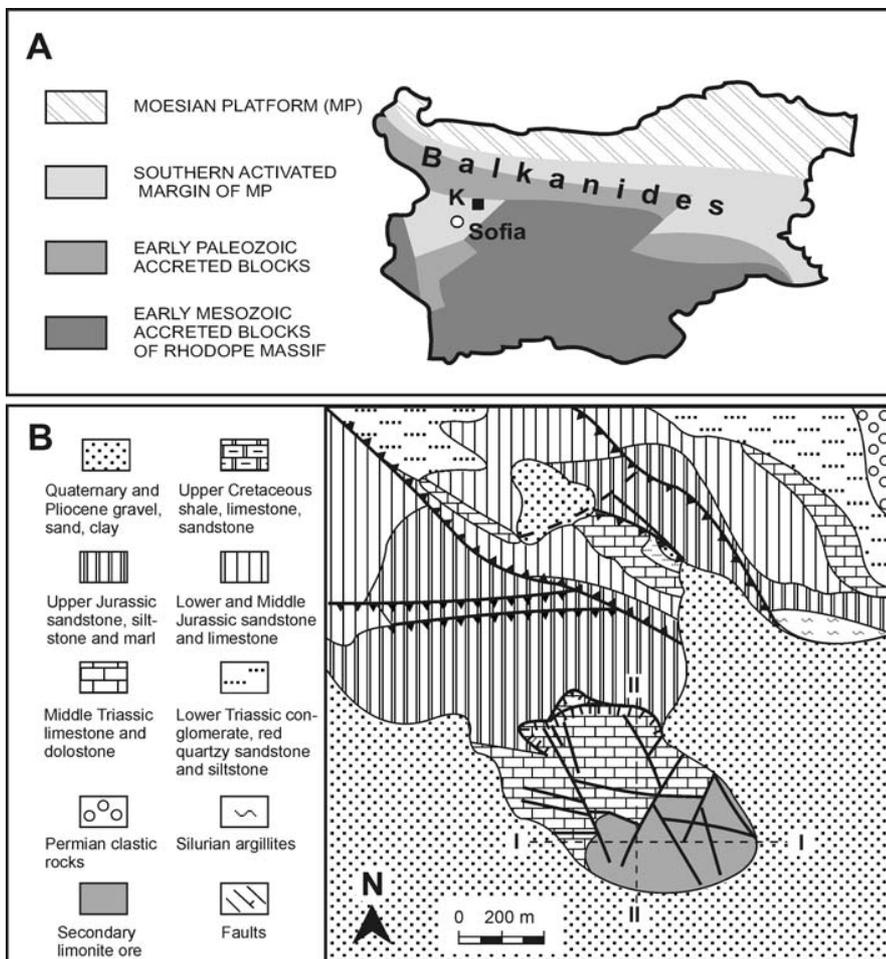
Fig. 1. Location (A) and geological map (B) of the Kremikovtsi ore field (after DAMYANOV, 1998).

crusts and crystal aggregates (ATANASSOV & VASSILE-VA, 1987).

Material and methods

Isomorphic substitutions in barite were studied in 38 samples by Infrared Spectroscopy (Perkin Elmer Spectrum One fourier transform infrared spectrophotometer, transmission mode, KBr/sample = 300mg/1mg pellets) and 7 samples by Raman Spectroscopy (SPEX Raman Spectrometer, Ar^+ laser excitation at 488.0 nm, P=150 mW, step 1 cm^{-1}, integration time 1s, powder sample in capillary tube).

The luminescence spectra of 7 barite samples were investigated under 2nd, 3rd and 4th YAG harmonics (532, 355 and 266 nm, correspondingly) pulsed lasers excitations. The spectra observed at the geometry of 90° were analyzed by INSTASPEC equipment, enabling time-resolved spectra acquisition with the following facilities: delay times and strobe pulse duration 20 ns – 9 ms, spectral detection range 300–900 nm (1200 channels, spectral resolution 0.5–1 nm, gratings with 300 and 600 lines/mm), detector type – intensified CCD matrix. The luminescence spectra were measured at room temperature (300 K).

X-Ray powder diffraction (Philips PW1710 diffractometer, Cu K_α, U=45 kV, I=40 mA, 2–70° 2θ, step 0.02° 2θ, 2 s/step; DRON M3, Co K_α, U=40 kV, I=40mA, 2–70° 2θ, step 0.05° 2θ) was used to control the purity of the barite samples.

Results and discussion

Barite has an orthorhombic structure (2/m 2/m 2/m), where the S is situated in tetrahedral coordination with O and the Ba is surrounded by 12 oxygens of 7 SO_4 tetrahedra (JAMES & WOOD, 1925). The BaO_{12} polyhedra and the SO_4 tetrahedra are edge-bound. The BaO_{12} polyhedra are irregular: six of the Ba–O distances are 2.77–2.81 Å, and the other 6 – 2.91–3.32 Å, which suggests a "sheet" structure parallel to {001}.

IR and Raman Spectroscopy

The sulfate group has 4 fundamental vibrational modes: one nondegenerate (ν_1), one doubly degenerate (ν_2), and two triply degenerate (ν_3 and ν_4). The IR spectrum of barite exhibits several significant bands: 2 strong bands corresponding to asymmetric stretching and bending (ν_3 and ν_4), and 2 weak ones – to symmetric stretching and bending (ν_1 and ν_2). The IR spectra of the studied endogene barites from the 3 main morphological types of bodies and from different mineral associations (Fig. 2) are very similar each other and to that reported by OMORI (1968; Table 1). Microprobe analyses show that Sr is the main isomorphic substitution for Ba in barite structure (SrO 0–4.5%; DIMOVA,

2006). ADLER & KERR (1965) found spectral shifts of the stretching modes (ν_3 and ν_1) to lower frequencies with increasing cation mass, such as the case of substitution Ba for Sr. The IR spectra of the studied endogene barites with different Sr contents (up to 4.5 % SrO) do not show any appreciable spectral shifts.
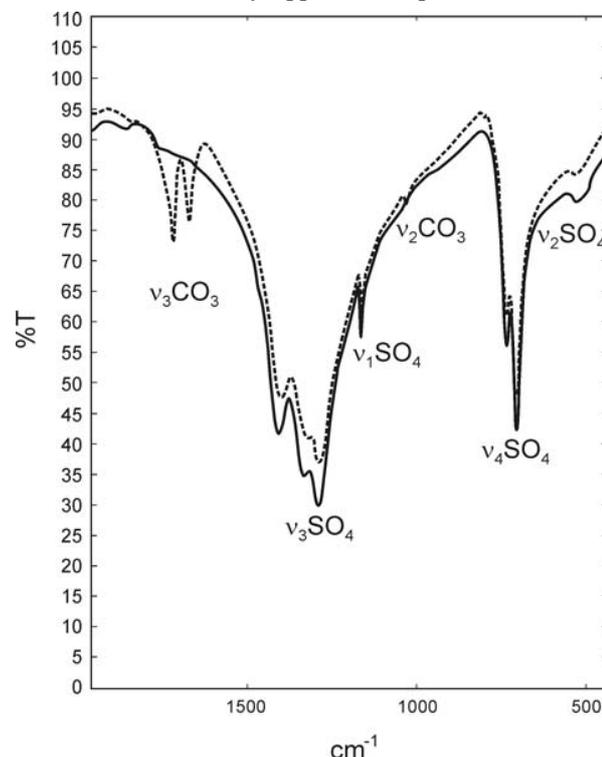
Fig. 2. IR spectra of endogene (bold line) and supergene (dashed line) barite from the Kremikovtsi deposit.

The IR spectra of the supergene barite (Fig. 2) are almost identical to those of the endogene ones in respect to the positions of the vibrational peaks, corresponding to the modes ν_1, ν_2, ν_4, except for a shift of 3 cm^{-1} for ν_3 (Table 1). A significant difference in the IR spectra of the supergene barite in comparison with the endogene one is the presence of additional bands at 1437, 1400 and 874 cm^{-1}, which correspond to the ν_3 and ν_1 modes of CO_3^{2-} in calcite (Fig. 2; Table 1). This suggests that the supergene barite has traces of calcite, undetectable by XRD (<2%).

All the Raman spectra of the studied barite samples are dominated by an intense ν_1 band (symmetric stretching of SO_4 tetrahedra) at 988 and 984 cm^{-1} for endogene and supergene barite, respectively (Fig. 3). The other characteristic bands, ν_2, ν_3 and ν_4, reported in the literature, are also present (Fig 3; Table 2). The Raman spectra of the supergene barites show additional bands at 1054, 710 and 270 cm^{-1} (Fig. 3; Table 2). The Raman studies support the suggestion that the supergene barite contains traces of calcite: ν_1(1086 cm^{-1}), which coincides with ν_3 of the SO_4 group and ν_4 (710 cm^{-1}) bands.

Table 1. Peak positions (cm⁻¹) of the Infrared modes of barite and calcite.

IR modes of SO_4^{2-}	Endogene barite, Kremikovtski deposit	Supergene barite, Kremikovtski deposit	Barite (OMORI, 1968)	IR modes of CO_3^{2-} in calcite (NAKAMOTO, 1997)
ν_1	982	982	980	
ν_2	467	468	470, 439	879
ν_3	1179, 1118, 1083	1176, 1115, 1182	1180, 1120, 1080	1429-1492
ν_4	610	610	633, 608	706
Additional bands		1437, 1400, 874		

Table 2. Peak positions (cm⁻¹) of the Raman modes of barite and calcite.

Raman modes of SO_4^{2-}	Endogene barite, Kremikovtski deposit	Supergene barite, Kremikovtski deposit	Barite (OMORI, 1968)	Raman modes of CO_3^{2-} in calcite (NAKAMOTO, 1997)
ν_1	988	984	987	1087
ν_2	462, 453	460, 454	460, 451	
ν_3	1167, 1140, 1084	1134, 1086	1167, 1140, 1083	1432
ν_4	647, 618	644, 618	646, 630, 617	714
Additional bands	1104	1054, 710, 270		
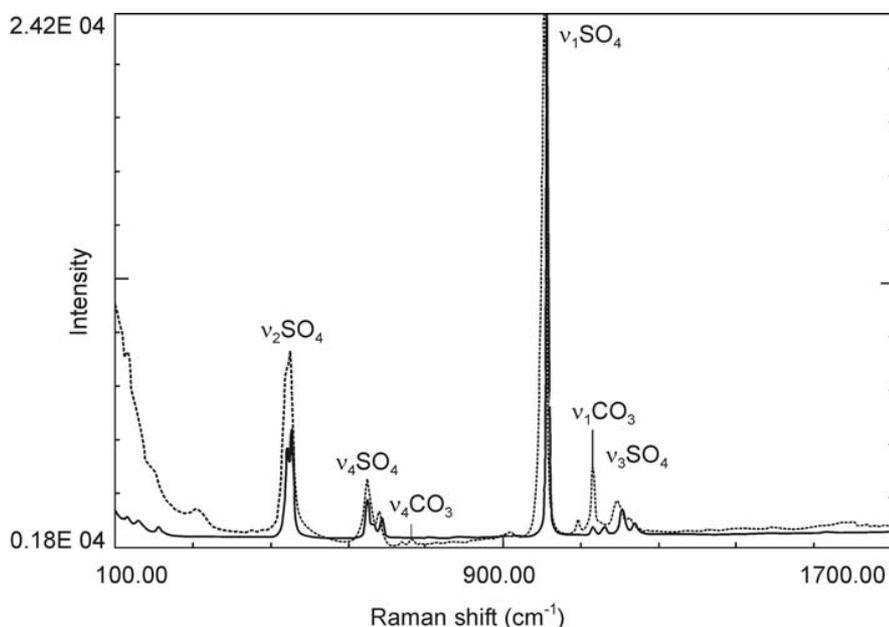
Fig. 3. Raman spectra of endogene (bold line) and supergene (dashed line) barite from the Kremikovtsi deposit.

Laser-induced time-resolved luminescence

Barite is one of the first luminescent materials from which the famous "Bologna stone" was obtained. It has been known for a long time that some barite specimens are fluorescent under UV exposure and emit white, yellow, green or orange light. In order to understand the nature of this phenomenon, the luminescence spectra of barite have been examined via UV, thermal and X-ray excitations. These studies allow the detection of the appearance of different luminescence bands from the UV to the red part of the spectrum.

Laser-induced time-resolved luminescence is a modern technique, which allows discrimination between centers with emission in the same spectral range, but with different decay times. The method involves recording the intensity in a specific time gate at a given delay after the excitation pulse, whereby both the delay and the gate width have to be carefully chosen. Such manipulation allows to be recorded separately the emissions corresponding to different decay times and to avoid the overlapping of the emissions produced from different centers. Laser-induced time-resolved luminescence of barites have detected and identified luminescence centers of Bi^{3+}, Bi^{2+}, Ag^+, Cu^+, REE^{3+} (Gaft *et*

al., 2001a; GAFT et al., 2005) in addition to UO_2^{2+} and Eu^{2+} revealed by Steady-State Photoluminescence (TARASHCHAN, 1978; GAFT et al., 1985; GOROBETS & ROGOJINE, 2001). Thus the information about the redox state of the different cations in the barite crystal lattice could throw more light on the origin of the barite.

The luminescence spectrum (excitation of 266 nm, without delay, broad gate of 9 ms) of the studied endogene barite contains 2 relatively narrow ultraviolet bands: one peaking at 306 nm and the other at 375 nm (Fig. 4A). The first band has a very short decay time and disappears after D = 50–100 ns. Such a combination of spectrum and decay time parameters is evidence that the luminescence is connected with Ce^{3+}. The emission of Ce^{3+} corresponds to transitions between $5d^1$ and $4f^1$ electronic configurations. The second band has a longer decay time of approximately 1 µs and belongs to Eu^{2+} (GAFT et al., 2005). The Emission spectra of Eu^{2+} result from electronic transitions between $4f^7$ and $4f^65d^1$ electronic configurations. After a delay of several µs, the Eu^{2+} emission becomes much weaker and very weak narrow lines appear, peaking at 488, 544 and 615 nm (Fig. 4B). These lines are connected with trivalent rare-earth elements, which are characterized by relatively long decay times of hundreds of µs: the first 2 lines certainly belong to Tb^{3+} and the last one is principally typical for Eu^{3+} (GAFT et al., 2005). While Eu^{2+} luminescence is common, Eu^{3+} emission is here detected for the first time in barite. Under excitation of 532 nm, a luminescence line at 615 nm dominates the spectrum, accompanied by several lines near 700 nm (Fig. 4C). Such a behavior confirms that Eu^{3+} is responsible for these luminescence lines. The emission of Eu^{3+} corresponds to f–f transitions – from the excited $^5D_0$ level to the ^7F_j (j=0, 1, 2, 3, 4, 5, 6) levels of the $4f^6$ configuration.

Some samples do not show Eu^{3+} luminescence. The relative intensities of Ce^{3+}, Eu^{2+} and Eu^{3+} in different samples are different: Ce^{3+} emission could be stronger than that of Eu^{2+}, while the luminescence of Eu^{3+} is relatively intensive. The different emission spectra at excitations at 266 and 532 nm suggest at least 2 structural positions for Eu^{3+} in the barite crystal lattice (Fig. 4C, D). Under excitation of 355 nm, a very broad orange-red band is detected (Fig. 4E), which was previously ascribed to Ag^+ luminescence (GAFT et al., 2005). One of the samples showed a relatively strong Ag^+ luminescence dominating the spectrum even with an excitation of 266 nm, which is not optimal for this emission (Fig. 4F). The emission bands of Ag^+ result from $d^9s–d^{10}$ transitions.

Under 266 nm excitation, without delay and with a broad gate of 9 ms, the luminescence spectrum contains 2 relatively narrow ultraviolet bands: one peaking at 320 nm and another at 375 nm (Fig. 4G). The latter band belongs to Eu^{2+}, while the origin of the first one is difficult to suggest. A similar emission has been found in synthetic barite artificially activated by Sn

(GAFT et al., 2005), but such an interpretation needs further support. The rather unusual narrow lines (at 370 and 391 nm) which appear in the luminescence spectrum with a longer delay of several µs (Fig. 4H) belong to trivalent rare-earth elements. They have been preliminary ascribed to violet-blue emission of Nd^{3+}, but this identification should be further clarified. The weak broad green band (at around 500 nm) may be related to uranyl emission, well known in barite (Fig. 4H).

The LITRL study of supergene barite did not show any luminescence. This could be connected with the lower impurity level in supergene minerals in general. A thermo-luminescence study of barite (KRIVOVICHEV, 1971) showed that the intensity of luminescence depends on the Sr concentrations in barite. The available data on the chemical composition of the Kremikovtsi supergene barite (ATANASSOV & VASSILEVA, 1987) showed very low Sr contents, which accounts for the absence of luminescence. Another possible explanation is that the luminescence is quenched by components with high-energy phonons, such as water or organic matter (GAFT et al., 2005).

The main prerequisite needed for a mineral to display luminescent properties, in the case that the luminescent centers are minor elements, is a similarity of the ionic radii and charges of the host and isomorphic elements. It is known that the luminescent centers Eu^{2+} (1.24–1.40 Å), Ce^{3+} (0.88–1.02 Å), Nd^{3+} (0.99–1.15 Å), Tb^{3+} (0.89–1.09 Å), Ag^+ (1.13–1.26 Å), Sn^{2+} (0.93 Å) substitute for Ba^{2+} (1.35–1.44 Å) or Sr^{2+} (1.10–1.27 Å), which are in 12-fold coordination in the barite structure (GOROBETS, 2002; GAFT et al., 2005; all ionic radii are for the 6-coordination form). A possible accommodation for the established in this study Eu^{3+} (0.97–1.13 Å) is also isomorphic substitution for Ba^{2+} or Sr^{2+}. The presence of uranyl molecules in barite is considered to be a result of chemical adsorption (GOROBETS, 2002).

Samples from both morphological types of endogene barite (veins and lenses, and veinlets and nests) fall into 2 groups: (1) barite with Eu^{2+} and Sn^{2+}(?), or Eu^{2+} and Ce^{3+}; (2) barite with Eu^{2+}, Eu^{3+} and Ce^{3+}. Barite samples from the first group contain isomorphic cations in their reduced form (Eu^{2+}, Sn^{2+}, Ce^{3+}), which implies that the barite precipitated from reduced fluids. A possible manner of this precipitation is conductive/convective cooling of the transporting fluid, which reaches the point of barite saturation with no substantial oxidation. The barite from the second group has reduced (Eu^{2+}, Ce^{3+}) as well as oxidized (Eu^{3+}) cations. This suggests that the barite from these samples precipitated from reduced transporting fluid subjected to oxidation. It can be speculated that both morphological types of barite are the result of conductive/convective cooling and mixing of hydrothermal fluid with seawater. This corroborates the most recent submarine hydrothermal model for the formation of the Kremikovtsi deposit (DAMYANOV, 1996a; DAMYANOV, 1998): sub- and on-seafloor precipitation upon cooling and mixing of hydrothermal fluid with seawater.
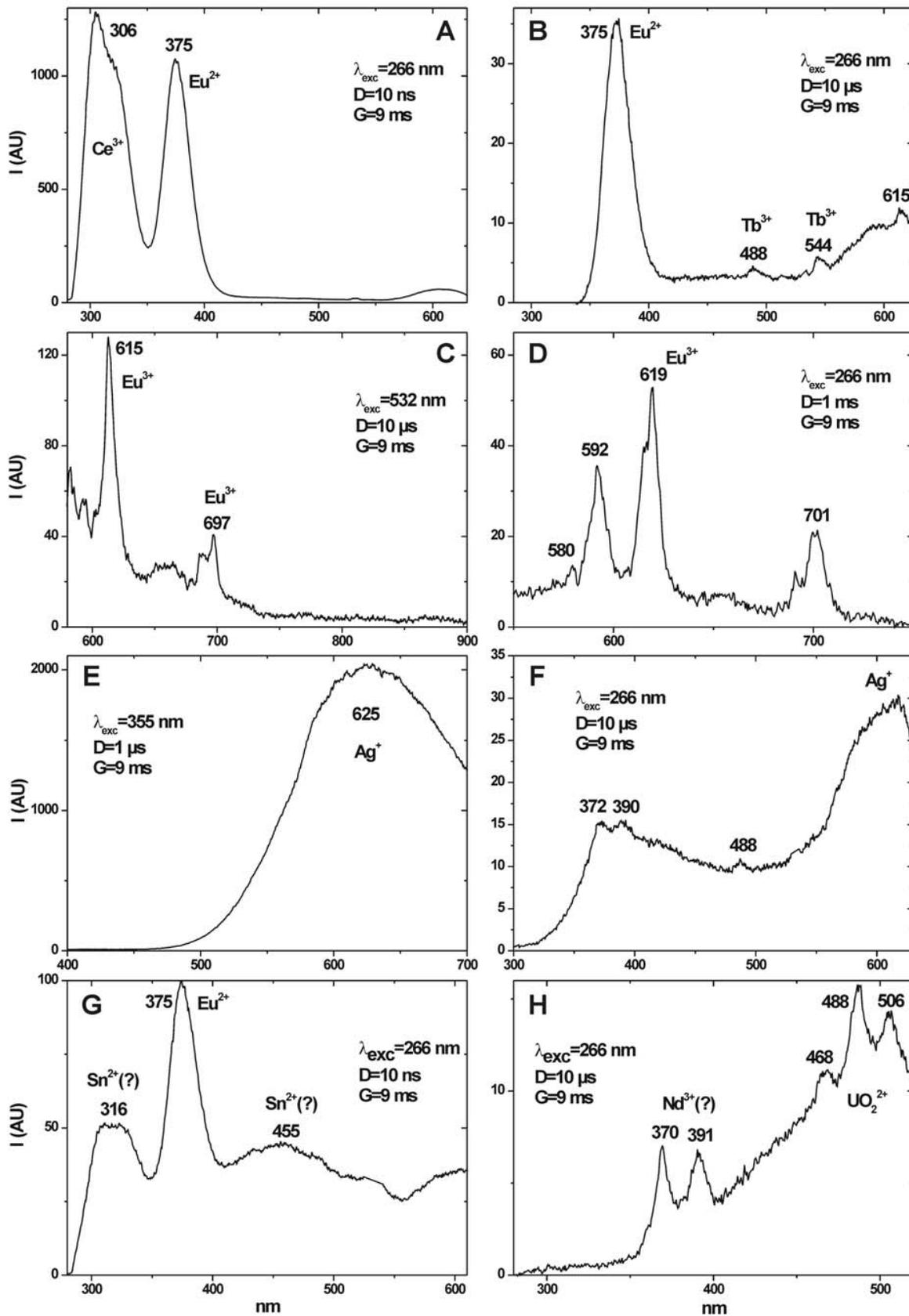
Fig. 4. Time-resolved luminescence spectra of endogenic barite from the Kremikovtsi deposit demonstrating different emission bands: (A) Ce^{3+}, Eu^{2+}; (B) Eu^{2+}, Tb^{3+}; (C) Eu^{3+}; (D) Eu^{3+}; (E) Ag^{+} (F) Ag^{+} (G) Eu^{2+}, Sn^{2+}; (H) Nd^{3+}, UO_2^{2+}.

Conclusions

The data obtained in the present study allow the following conclusions to be drawn:

(1) There is no structural difference depending on the varying Sr content (0–4.5 wt.%) in all the morphologic types of endogene barite, according to the IR and Raman studies. Supergene barite shows IR and Raman spectra identical to those of the endogene one with the only difference being the presence of traces of calcite.

(2) The laser-induced, time-resolved luminescence technique is a suitable tool for the identification of rare-earths (undetectable with conventional methods) in barite and the discrimination of their oxidation states.

(3) Along with the common Eu^{2+} luminescence, the emission of Eu^{3+} was detected for the first time in barite. There are at least 2 structural positions for Eu^{3+} in the barite crystal lattice.

(4) It seems that the endogene barite in the Kremikovtsi deposit was precipitated from reduced fluids subjected to cooling (conductive/convective) and oxidation (mixing with seawater).

Acknowledgements

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Резиме

Спектроскопско проучавање барита из лежишта Кремиковци (Бугарска) са импликацијама његовог порекла

Лежиште гвожђа(+Mn)-барита-сулфида Кремиковци у Бугарској садржи различите метале и велике резерве руде барита. Пошто се лежиште експлоатисало углавном због гвожђа, претежно су вршена испитивања гвоздене руде. Постоји само неколико минералошких и геохемијских студија барита. Циљ овог проучавања је боље упознавање са структуром и катјонском валентношћу барита са импликацијама његовог порекла. Различити генетски (ендогени и супергени) и морфолошки (жице и сочива, као и жилице и гнезда) типови барита испи-

тивани су применом спектроскопских метода ласерски редуковане луминесценције (LITRL), инфрацрвене анализе (IR) и Рамонове анализе.

Инфрацрвени спектри ендогеног барита сасвим су слични спектрима објављеним у литератури. Не постоји структурна разлика која зависи од променљивог садржаја Sr (0–4,5 теж.%) ни у једном морфолошком типу ендогеног барита. Инфрацрвени спектри супергеног барита скоро су идентични спектрима ендогеног барита у погледу положаја вибрационих пикова ν_1, ν_2 и ν_4 SO_4^{2-}, осим за помаке од 3 cm^{-1} код ν_3. Ти спектри су показивали присуство додатних трака, које су блиске пиковима ν_3 и ν_1 CO_3^{2-} у калциту. Раманова проучавања иду у прилог наговештаја да супергени барит садржи трагове калцита.

Савремена техника LITRL, као погодан начин утврђивања ретких земаља (које се не могу открити класичним методима) и разликовања њихових степена оксидације, омогућила је утврђивање неколико центара луминесценције у ендогеном бариту. Луминесценција Eu^{3+} је по први пут утврђена у бариту. Различити емисиони спектри при побуди од 266 и 532 nm указују на присуство бар два структурна положаја Eu^{3+} у кристалној решетки барита. Луминесцентни спектри су такође открили доста необичну љубичасто-плаву емисију Nd^{3+}, која се обично јавља у опсегу инфрацрвеног спектра, као и емисије Ce^{3+}, Eu^{2+}, Tb^{3+}, Ag^+, Sn^{2+}(?) и UO_2^{2+}.

Степен оксидације катијона изоморфно присутних у кристалној решетки барита указује да је ендогени барит у лежишту Кремиковци наталожен из редукованих флуида за које се претпоставља да су били изложени хлађењу (кондуктивно односно конвективно) и оксидацији (мешањем са морском водом).