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The luminescence of Bi, Ag and Cu in natural and synthetic barite BaSO₄

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Abstract

The time-resolved laser-induced luminescence of natural barite BaSO₄ is compared with synthetically prepared BaSO₄–Bi, BaSO₄–Ag and BaSO₄–Cu. It is deduced that in natural barite the narrow orange band with $\lambda_{\text{max}} = 625$ nm, $\Delta = 40$ nm and $\tau = 5$ μ s is connected with Bi²⁺ center. The narrow violet band with $\lambda_{\text{max}} = 625$ nm, $\Delta = 35$ nm and $\tau = 1.7$ ms is connected with Bi³⁺ center. The broad red band with $\lambda_{\text{max}} = 635$ nm, $\Delta = 140$ nm and $\tau = 270$ μ s is connected with Ag⁺ center. The broad red band with $\lambda_{\text{max}} = 750$ nm, $\Delta = 110$ nm and $\tau = 350$ μ s is connected with Cu⁺ center. Such luminescence centers are firstly considered in minerals. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Barite, is a barium sulfate, BaSO₄, with orthorhombic structure (2/m 2/m 2/m) where the sulfur is situated in tetrahedral coordination with oxygen, and barium in 12-fold coordination with oxygen. Mineral barite is one of the first luminescent materials from which the famous “Bologna stone” was obtained. Nevertheless, till today the understanding of natural barite luminescence is very scarce. It has been known for a long time that some specimens of barite 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 were examined via UV, thermal and X-ray exci-

tations. These studies allowed the detection of the appearance of different luminescence bands from the UV to the red part of the spectrum [1–3]. However, only UO₂²⁺ and Eu²⁺ luminescence centers have been confidently identified.

The purpose of this work is to examine the orange luminescence of barite exhibiting spectral-kinetic characteristics very unusual for minerals. Here, we applied laser-induced time-resolved luminescence measurements, 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 where both the delay and the gate width have to be carefully chosen. Such manipulation allows us to record separately the emissions corresponding to different decay times and to avoid the overlapping of the emissions produced from different centers without any peak deconvolution.

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2. Experimental

2.1. Spectroscopy

The luminescence spectra were investigated under excimer UV (308 nm), nitrogen (337 nm) and third and fourth YAG harmonics (355 and 266 nm, respectively) pulsed lasers excitations which deliver pulses of 10 ns duration and 0.1 cm^{-1} spectral width. The spectra observed at the geometry of 90° were analyzed by INSTASPEC equipment enabling time-resolving 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 temperatures from 4.2 to 300 K.

2.2. Samples

The natural barite in this study consisted of 9 samples from different origin (Table 1) with intensive orange luminescence. The samples were checked by IR, micro-Raman and X-ray diffraction methods to assure that they do not contain impurities of foreign minerals, which may serve as host matrix for luminescence centers.

For the correct interpretation of orange luminescence, synthetic barite standards doped with potential luminogens were prepared. In order to obtain the clear solution, 4.886 g of barium chlo-

ride $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (analytical grade) was dissolved in 50 ml of water by stirring during 20 min on a hot plate (80°C). The corresponding amounts of luminogens were added to the solution at the same temperature by stirring during 10 min. In another glass 3.168 g of ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$ (special enzyme grade) solution in 20 ml of water was prepared by stirring during 10 min on a hot plate (80°C). The two solutions were mixed under intensive stirring on a hot plate at the boiling temperature. After evaporating 80% of water, the wet precipitate was placed into a crucible and put in an oven at 300°C for the final evaporation. The last step was thermal treatment at 700°C during 15 min. The samples were shown to consist of a single barite phase by X-ray powder diffraction.

2.3. Inducted-coupled plasma analyses

The concentrations of impurities were analyzed by inductive-coupled plasma (ICP) method (Table 1). In order to bring barite into solution, Ba and SO_4 must be separated from each other after the fusion. The barite samples were fused with Na_2CO_3 in the ratio of 5 g Na_2CO_3 to 1 g of the sample. The fusion was done in Pt-crucible for about 30 min. After cooling, the crucible was put in the beaker and the melt was leached by distilled water. After cleaning, the whole content of the crucible was filtered, thus separating between the precipitate, which contains the Ba and BaCO_3 , and the solution that contains the sulfate. The precipitate was washed thoroughly with double distilled

Table 1
Impurities concentrations (ppm) in barite under investigation ^a

Origin	Ag	Bi	Cu	Ti	Fe	Mn	Al	Pb	Sn	U	Sr
Israel	0.2	0.2	55	6.5	430	400	80	3.0	–	0.2	9700
Spain	–	–	3.5	0.5	75	6.0	20	1.0	–	0.2	1180
Cluny (France)	1.2	0.3	13	5.0	3900	2.9	500	220	0.4	0.3	10100
France 1	1.5	–	3.3	2.7	950	3.5	5.0	62	–	0.1	760
France 2	21	–	5.0	–	45	2.1	120	1.5	–	–	685
France 3	4	–	3.6	1.3	230	6.5	60	0.8	–	0.2	590
Felsobanya (Rumania)	0.4	–	1.2	1.0	70	2.2	–	1.0	1.5	–	10300
Rumania	–	–	3.2	2.4	360	5.2	–	5.0	–	2.0	530
Cumberland (England)	0.6	–	5.7	1.7	120	13.0	200	9500	–	2.0	390

^a NB. Emphasized are the samples with strong orange luminescence.

water and dissolved in pure grade Nitric Acid – “Bakerinstra-Analyzed Reagent – for trace metal analyses”. The solution was brought to 100 ml volume. The filtrate, containing the sulfate fraction was brought to 200 ml volume. BaSO_4 “Cpecpure” grade, supplied by Jonson Matthey Chemicals, was analyzed along with the samples, as a blank, to overcome the interference problems. The concentrations of Al, Cu, Fe, Mn, Sr, Ti were determined by ICP -atomic-emission-spectroscopy (ICP-AES), with the Perkin–Elmer OPTIMA-3300 Instrument. Each analyzed sample solution contained 5 mg/l of Sc as an internal standard. The concentrations of Ag, Bi, Pb, Sn and U were determined by ICP-mass-spectroscopy (ICP-MS), with the Perkin–Elmer/Sciex Elan-6000 Instrument. The work was done with flow-injection system (FIAS 400, Perkin–Elmer), a technique in which only 80 μg are introduced into the instrument, giving a transient signal. This enables the introduction of relatively more concentrated solutions, without further dilution which lowers the trace elements concentrations. The quantities of 10 $\mu\text{g/l}$ of Rc and Rh were put into the analyzed samples, as an internal standards, Re for Bi, Pb and U and Rhg for Ag and Sn.

Both the acid solutions, containing the Ba fraction, and the water solutions, containing the sulfate fraction, were analyzed for all the elements. Almost in all the elements analyzed, the major part of the concentration was found in the Ba fraction and the minor part – in the sulfate fraction. The results are the sum of the concentrations in the two fractions.

3. Results and discussion

3.1. Natural samples with orange–red luminescence

Fig. 1 represents typical laser-induced luminescence spectra recorded from natural barite with orange luminescence. At room temperature under 308, 337 and 355 nm excitations orange luminescence consists of very broad band peaking at 635 nm with half-width of approximately $\Delta = 150$ nm (Fig. 1(a) and (b)). At lower temperatures up to liquid helium the spectrum is very similar and only

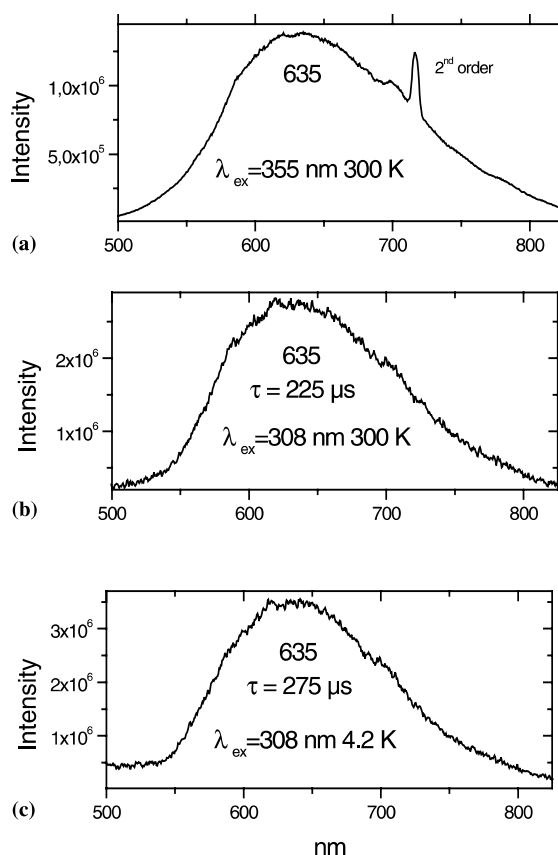


Fig. 1. Luminescence spectra of mineral barite under different laser excitations at different temperatures: (a) $\lambda_{\text{ex}} = 355$ nm, $T = 300$ K; (b) $\lambda_{\text{ex}} = 308$ nm, $T = 300$ K; (c) $\lambda_{\text{ex}} = 308$ nm, $T = 4.2$ K. (In (a), the second order of the laser pump line is shown to give an approximate evaluation of the luminescence intensity. We have adapted the same approach for the other luminescence spectra.)

the half-width of $\Delta = 130$ nm becomes a little narrower (Fig. 1(c)). At all temperatures the spectra are not depending on delay times and gate widths. The possible conclusion is that only one luminescence center is responsible for this orange band. Decay time of luminescence is approximately 225 μs at 300 K and 275 μs at 4.2 K.

The spectrum is absolutely different under short wave 266 nm excitation (Fig. 2). Now two bands are detected: the intensive blue one with very short decay time of 100 ns and the relatively weak narrow orange one with half-width of 30 nm and decay time of 5 μs . In order to present both bands

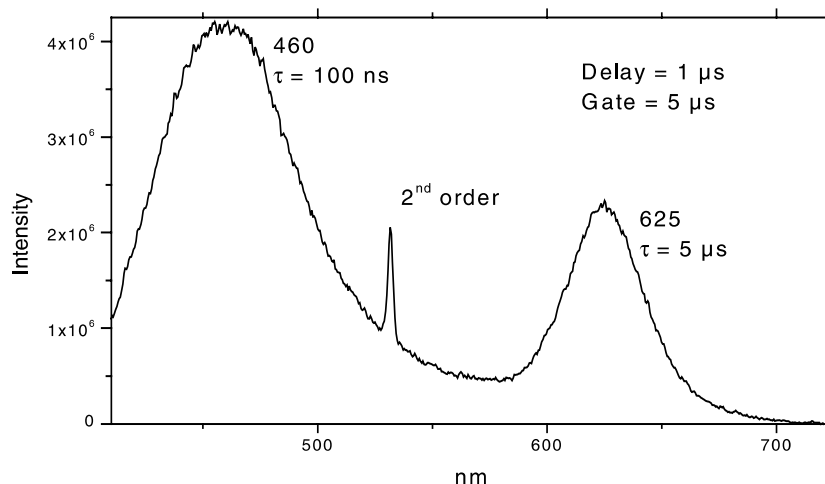


Fig. 2. Luminescence spectra of mineral barite under $\lambda_{\text{ex}} = 266$ nm at 300 K.

in comparable magnitudes, the 1 μs delay is used to diminish the intensity of the short lived blue emission. The narrow orange band disappears after heating in air at 600°C. Such luminescence is not detected under longer UV laser lines.

Let us first discuss why the orange luminescence cannot be assigned to some obvious reasons. The host itself may be excluded, because pure barite is not luminescent. The usual luminescence center in minerals, which are responsible for broad orange bands with relatively long decay time, is Mn^{2+} . This possibility may be excluded also for the following reasons. ICP data really reveals Mn impurity presence (Table 1), but the correlation between Mn concentration and orange luminescence intensity is absent. For example, two samples with strongest orange luminescence have 3.5 and 400 ppm of Mn. Nevertheless, we prepared and studied synthetic barite artificially activated by Mn. As a result only extremely weak green band with very long decay time of 1 ms is seen, which is not detected yet in natural samples. According to EPR data ionic impurities of 4-fold coordinated Mn^{5+} were detected in barite [4] and it is possible to suppose that it is the main form of Mn here.

Other possible centers of broad band orange luminescence are Fe^{3+} in tetrahedral coordination and Cr^{3+} in octahedral one. Tetrahedral surrounding presents in barite structure but $\text{Fe}^{3+}\text{--S}^{6+}$

substitution is very difficult to suppose. Octahedral coordination is absent in barite structure and in addition ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$ broad band of Cr^{3+} ion is located at longer wavelength than 635 nm as it is observed with barite. The iron presence in ICP data is evidently connected with micro-impurities of iron minerals, which is usual for natural barite. It is also possible to suppose that Fe is accommodated in the Fe^{2+} form, which has not luminescence in the visible range. Other d^{10} ions, such as Ti^{3+} and Ni^{2+} with possible red luminescence, have ionic radii of 81 and 83 pm, respectively, which are small compared to 156 ppm of Ba^{2+} . ICP data confirm the absence of Ni in natural barite, while the minor quantities of Ti may be connected to Ti^{4+} with possible blue luminescence.

3.2. $\text{BaSO}_4\text{--Bi}$

Thus other interpretations are needed. It is interesting to note that while narrow orange band is firstly detected in natural barite, it has been reported in 1886 for synthetic $\text{BaSO}_4\text{:Bi}$ [5]. Half a century later this was confirmed and connected with Bi^{3+} luminescence [6]. Another half a century later the new interpretation has been done and it was assumed that the luminescence center is Bi^{2+} [7].

We investigated laser-induced time-resolved luminescence of synthetic $\text{BaSO}_4\text{--Bi}$. Under 266 nm

excitation the narrow orange band, exactly similar to those in natural barite appears (Fig. 3(a)), which is evidently connected with Bi activator. Besides short UV excitation, orange luminescence may be excited in the yellow band peaking at 580 nm (Fig. 3(b)).

Under 308, 337 and 355 nm excitations of BaSO₄:Bi the blue–green luminescence appears, which is strongly temperature dependent. At room temperature the luminescence intensity is very weak. It consists of violet band at 421 nm with long decay time of 1.7 ms and green band at 500 nm with very short decay time of 2 μ s. To be represented in clear form, the violet band is detected with delay of 10 μ s in order to quench the shorter luminescence, while the green band is detected with narrow gate of 100 μ s to quench the longer emission (Fig. 4(a) and (b)). At liquid nitrogen temperature the luminescence intensity is approximately 20 times stronger and both emission bands become much broader and shift to long

wavelength direction (Fig. 4(c) and (d)). The long lived violet band does not change its non-elemental form with different delay times up to 8 ms. At 50 K temperature the intensity of the violet band remains the same and it becomes narrower, while the green band intensity is diminished (Fig. 4(e) and (f)). At liquid helium temperature the violet band becomes even narrower, shifts substantially in the short wavelength direction and its decay time of 3.1 ms becomes much longer, while the green emission is practically disappears (Fig. 4(g) and (h)).

After thermal treatment of the sample at 800°C the violet band disappears and the only one peaking at 575 nm is detected, which is practically absent at room temperature, but is very strong at liquid nitrogen and helium (Fig. 5). Decay time of such yellow luminescence of 2.5 μ s is relatively short.

It is well known that Bi produces different kinds of luminescence in a large number of substances, even in its own compounds [8,9]. We are therefore inclined to attribute all detected bands to electronic transitions in the different Bi-based centers.

The narrow orange band in BaSO₄:Bi was previously ascribed to Bi³⁺ [6] or Bi²⁺ [7]. The last one was firstly proposed as luminescence center in BaSO₄, but recently its existence was confirmed in M²⁺BPO₅ (M = Ba, Sr, Ca) [10]. In attempt to clarify this problem we used step-like thermal treatment in air in order to stimulate Bi oxidation with possible change of valence state. In natural barite the narrow orange band totally disappeared after heating at 700°C. Such a behavior usually evidences that emission is connected with luminescence center in the lowest valence state, namely Bi²⁺. Its electron configuration is (6s)²(6p)¹, yielding a ²P_{1/2} ground state and a crystal field split ²P_{3/2} excited state [7]. Because the emission is a 6p interconfigurational transition ²P_{3/2}–²P_{1/2}, which is confirmed by the yellow excitation band presence, it is formally parity forbidden which is well agreed with the observed decay time of 5 μ s (Fig. 6(a)). Since the uneven crystal-field terms mix with the (6s)²(7s)¹, ²S_{1/2} and the ²P_{3/2} and ²P_{1/2} states, the parity selection rule becomes partly lifted. The excitation transition ²P_{1/2}–²S_{1/2} is

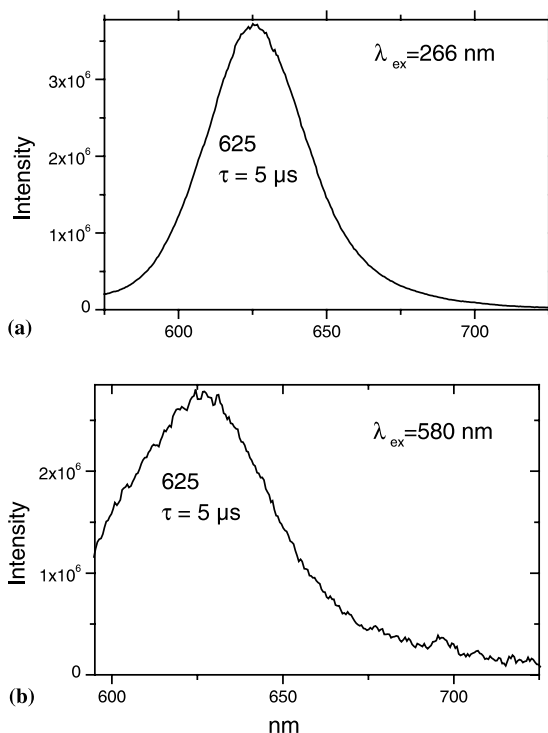


Fig. 3. Luminescence spectra of synthetic BaSO₄:Bi under $\lambda_{\text{ex}} = 266$ nm (a) and $\lambda_{\text{ex}} = 580$ nm (b).

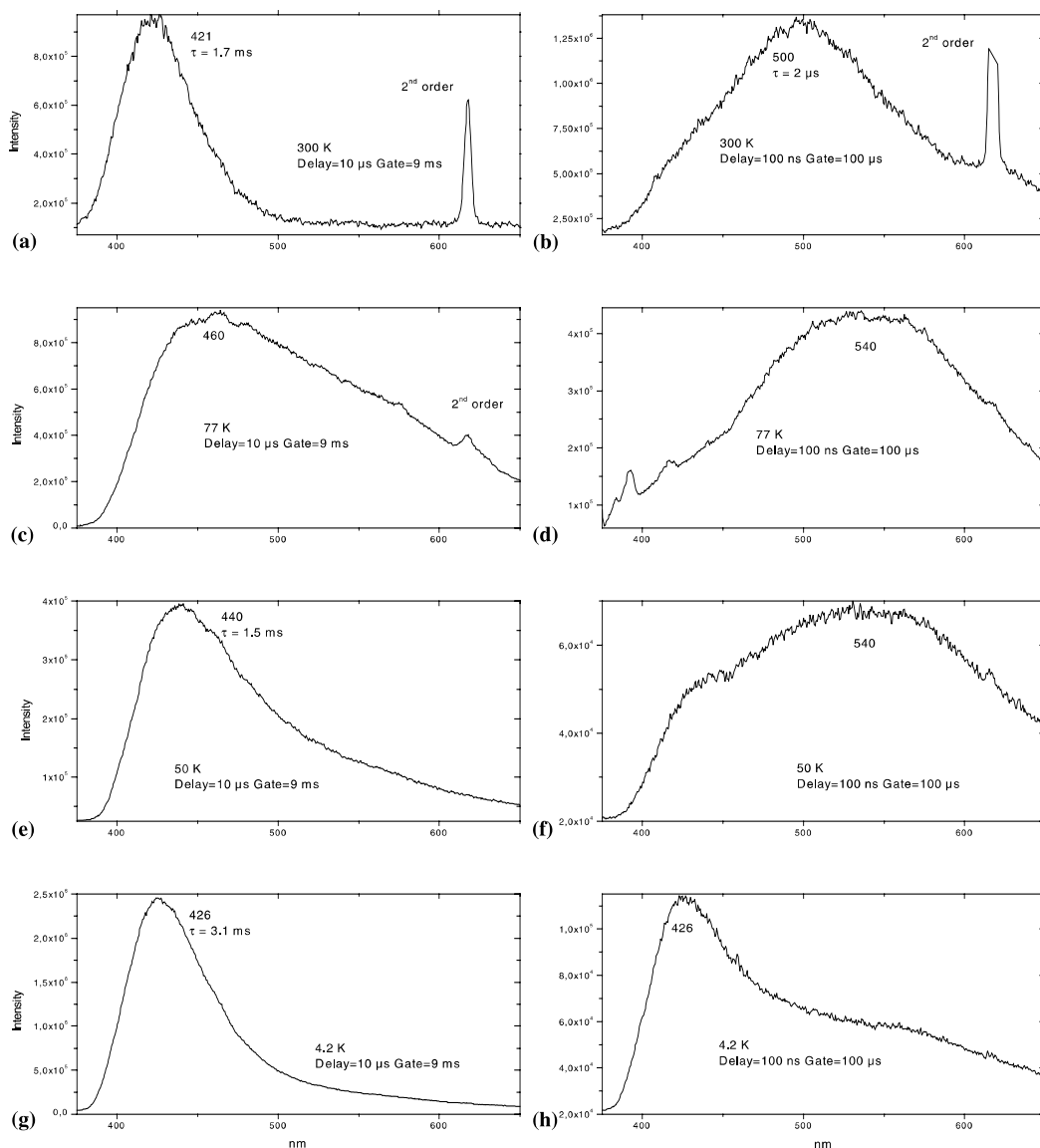


Fig. 4. Luminescence spectra of synthetic $\text{BaSO}_4\text{-Bi}$ under $\lambda_{\text{ex}} = 308$ nm with different combinations of delay time and gate width to detect long lived and short lived emission bands: 300 K (a, b), 77 K (c, d), 50 K (e, f) and 4.2 K (g, h).

allowed one and it demands photons with higher energy [11], which corresponds to our case where narrow orange band is excited only by short wave 266 nm laser beam. 308, 337 and 355 nm laser lines do not excite such luminescence, but it is detected under such excitations in BaSO_4 , simultaneously activated by Bi and Sn and is evidently connected with energy migration from Sn to Bi.

The luminescence of Bi^{3+} is quite diverse and depends strongly on the host lattice [8,9]. It belongs to s^2 ions, where the filled s shell of a free ion gives rise to a 1S_0 ground state (Fig. 6(b)). The excited sp state gives a triplet $^3P_{0,1,2}$ for spins parallel and a singlet 1P_1 for spins antiparallel. In view of the selection rules, only the transitions between the singlets are allowed. For the heavy

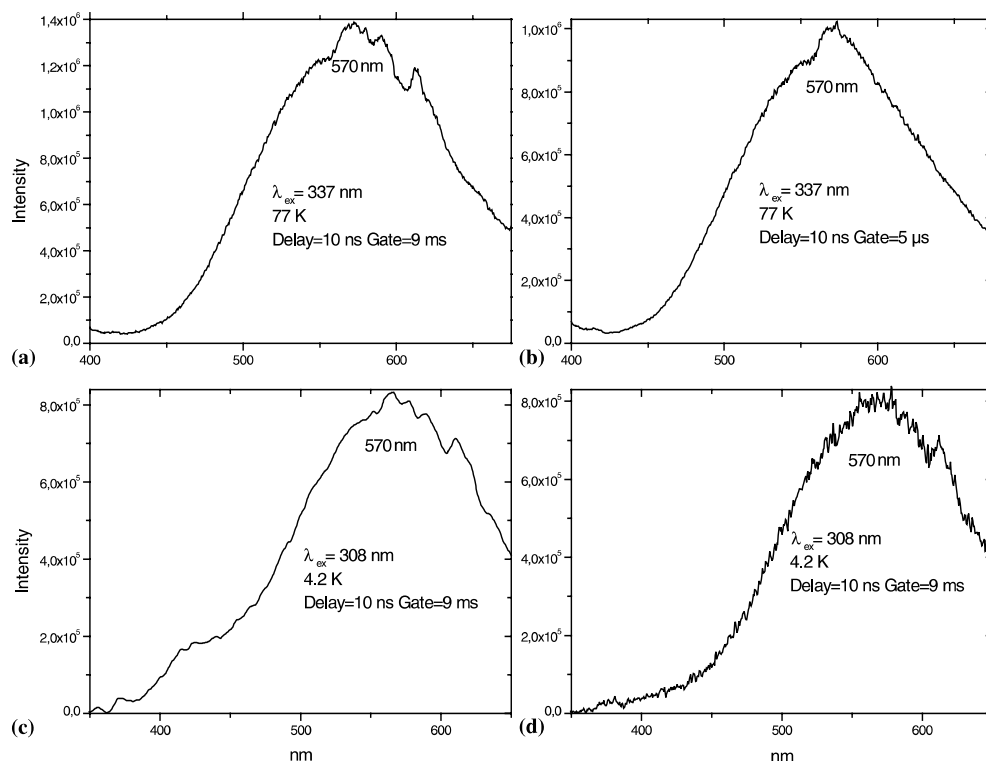


Fig. 5. Luminescence spectra of synthetic $\text{BaSO}_4\text{-Bi}$ after heating in air at 800°C : $\lambda_{\text{ex}} = 337 \text{ nm}$ at 77 K (a, b) and 308 nm at 4.2 K (c, d).

$6s^2 \text{Bi}^{3+}$ the transitions between the ground state and the $^3\text{P}_1$ state becomes additionally allowed by spin–orbit mixing of the $^3\text{P}_1$ and $^1\text{P}_1$ states. After excitation at low temperature, the system relaxes to the lowest excited state. Consequently, the emission at low temperatures can be ascribed to the forbidden transition $^3\text{P}_0 \rightarrow ^1\text{S}_0$ and has a long decay time. Nevertheless, both $^3\text{P}_1$ and $^3\text{P}_0$ are emitting levels and they are very close so that at higher temperatures the luminescence from $^3\text{P}_1$ level may appear with similar spectrum, but with shorter decay. It is clearly seen that the violet luminescence has suitable characteristics and is mostly probable connected with $^3\text{P}_{0,1} \rightarrow ^1\text{S}_0$ transitions in Bi^{3+} center.

The green emission is most probably also connected with Bi^{3+} center. It may be explained by splitting of $^3\text{T}_{1u}$ excited state [8] (Fig. 6(b)). At very low temperature the T minima are preferentially populated and the barrier between T and X is so

high that only a small part of the system arrives at the X minimum and the green band is practically absent. As the temperature is raised T populates X and both violet and green bands have the similar intensities.

The only possible position for Bi^{3+} and Bi^{2+} in barite lattice is in the Ba^{2+} site. The Ba ions in the structure of barite lie on the mirror planes and link the sulfate ions in such a way that twelve oxygen atoms coordinate each Ba. The exact ionic radius for Ba^{2+} in such coordination is unknown, but for coordination number 8 it is equal to 156 pm. Bi^{3+} in such coordination has ionic radius of 131 pm, which is very close. The exact ionic radius for Bi^{2+} is also unknown, but it has to be even bigger than for Bi^{3+} , which is compatible with big ion Ba^{2+} , especially for isomorphous substitution, when the charge compensation is not needed. The big half-width of Bi^{3+} luminescence band of 75 nm in barite is not surprising. It was observed that

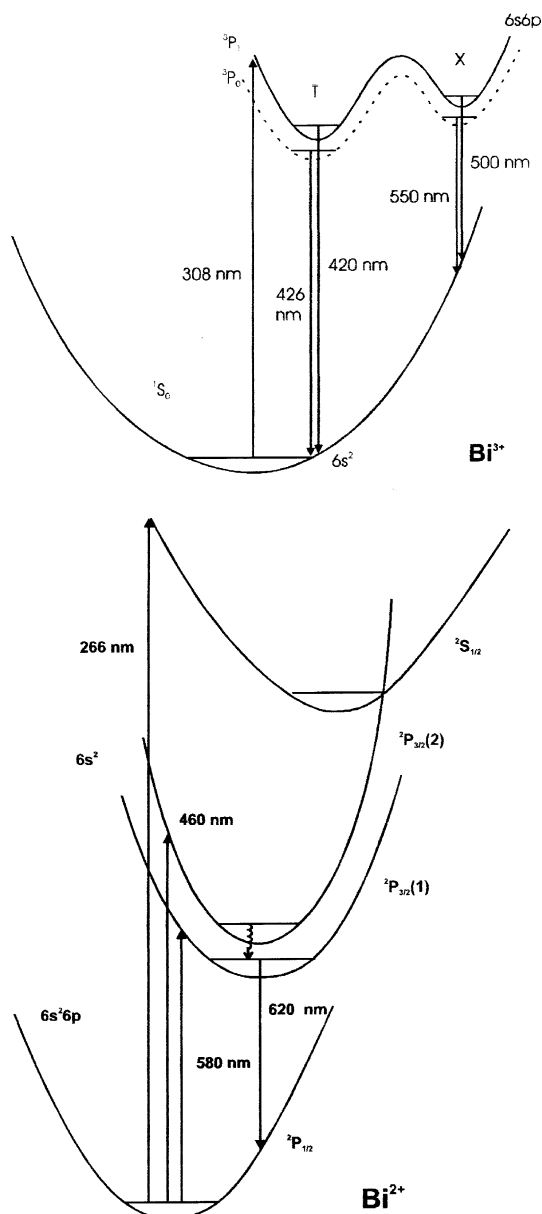


Fig. 6. Configurational coordinate diagram showing emission and excitation transitions of Bi^{3+} and Bi^{2+} .

when Bi^{3+} is a substitute for big ion the Stokes shift increases and very broad luminescence bands take place [8,9]. The large variation of Bi^{3+} luminescence is ascribed to the amount of space available for the Bi^{3+} ion in the lattice. The Bi^{3+} ion in Ba position with coordination number 12 has enough

space for relaxation after excitation with resulting large Stokes shift and half-width. The magnitude of this shift depends on the details of vibrational relaxation in the excited and ground states, which, in turn depend on the interaction of the emitting ion with the adjacent coordination ions in the structure. The lower Stokes shift and half-width for Bi^{2+} may indicate the weak interaction case where configuration curves are essentially flat.

The yellow band at 575 nm in the $\text{BaSO}_4:\text{Bi}$ heated at 800°C may be ascribed to the so-called D excited state, which is considered to be charge transfer in nature, but the exact origin is still unsure [12]. The excited 3P_1 and D levels are separated by a potential barrier, which can be overcome by thermal energy. As it was demonstrated for $\text{BaSO}_4:\text{Pb}^{2+}$, which is iso-electronic with Bi^{3+} , the high coordination number of barite destabilizes the levels of the sp configuration relative to the D levels. The large Ba^{2+} site of the barite host lattice makes the D emission more probable [13].

Nevertheless, our data on step-like oxidizing heating makes another explanation possible. The

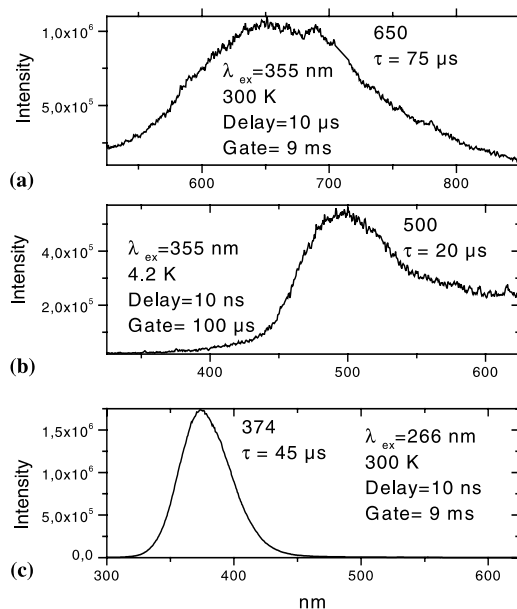


Fig. 7. Luminescence spectra of synthetic $\text{BaSO}_4\text{--Ag}$ showing three different emission bands: orange (a), green (b) and ultra-violet (c).

yellow band dominates after barite oxidizing heating in air at high temperature. Thus luminescence of Bi in higher valence state, namely Bi^{5+} , may be principally proposed. Such valence is possible for Bi and its configuration is $5d^{10}$. Luminescence from higher valence ions with d^{10} configuration has been questioned for a long time. Nowadays there exists strong evidence for such a luminescence [9]. The higher valence ions include Sb^{5+} , which is very close to Bi^{5+} [14]. The Stokes shifts are very large and the spectral bands are broad, indicating a drastic rearrangement in the excited state upon excitation. The nature of this emission is not yet completely clear, but probably it contains a certain amount of $\text{O}^{2-}\text{--Sb}^{5+}$ charge transfer, next to $2p\text{--}3s$ excitation on the O^{2-} ion. We have to add that very small ionic radius of 74 pm for Bi^{5+} is known in octahedral coordination so that we should assume the same type of con-

figuration by only taking account of the first six oxygen atoms within the 12 coordinated Ba^{2+} site, which is obviously questionable without any other data.

3.3. $\text{BaSO}_4\text{--Ag}^+$ and $\text{BaSO}_4\text{--Cu}^+$

In order to check the possibility of d^{10} -ions luminescence in barite lattice, the activation by Ag and Cu was accomplished. Another reason was that in all natural barite samples the Ag and Cu impurities have been determined by ICP analysis (Table 1). Relatively high Cu concentration of

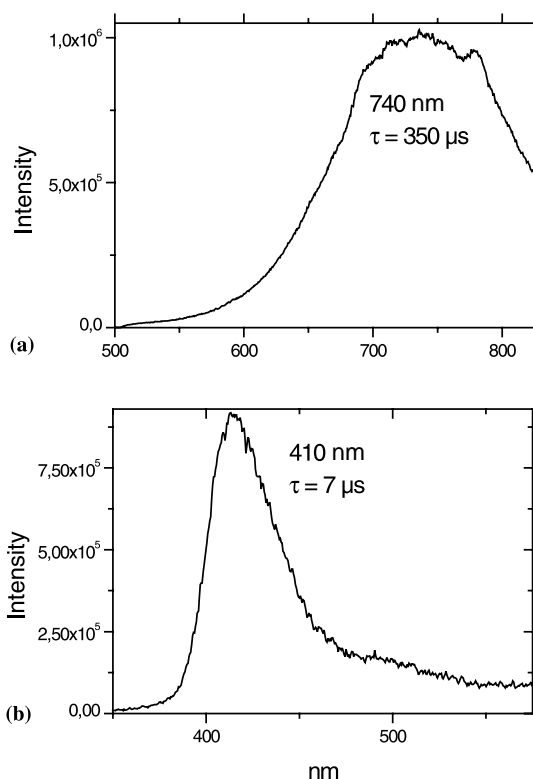


Fig. 8. Luminescence spectra of synthetic $\text{BaSO}_4\text{--Cu}$ under $\lambda_{\text{ex}} = 308 \text{ nm}$ at 300 K showing two different emission bands: red (a) and violet (b).

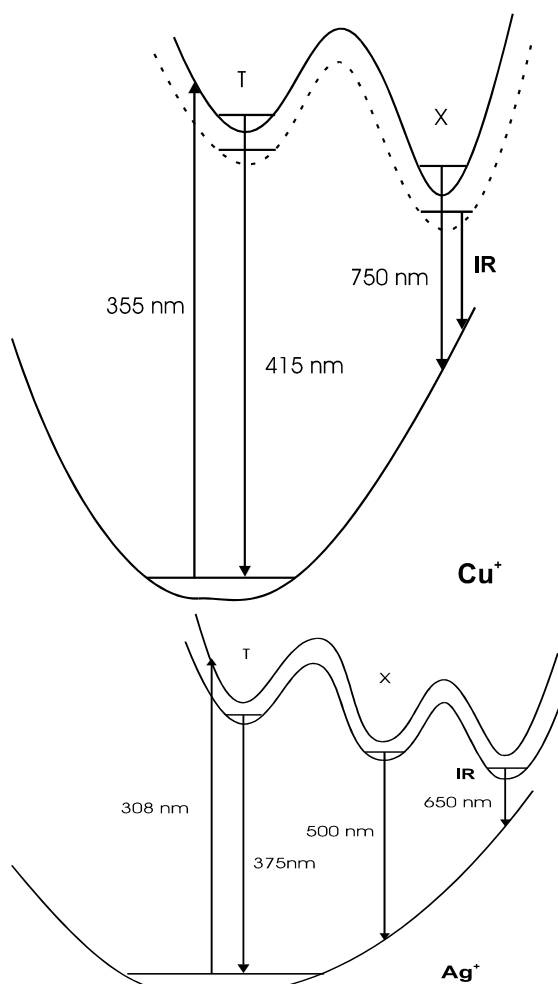


Fig. 9. Configurational coordinate diagram showing emission and excitation transitions of Cu^+ and Ag^+ .

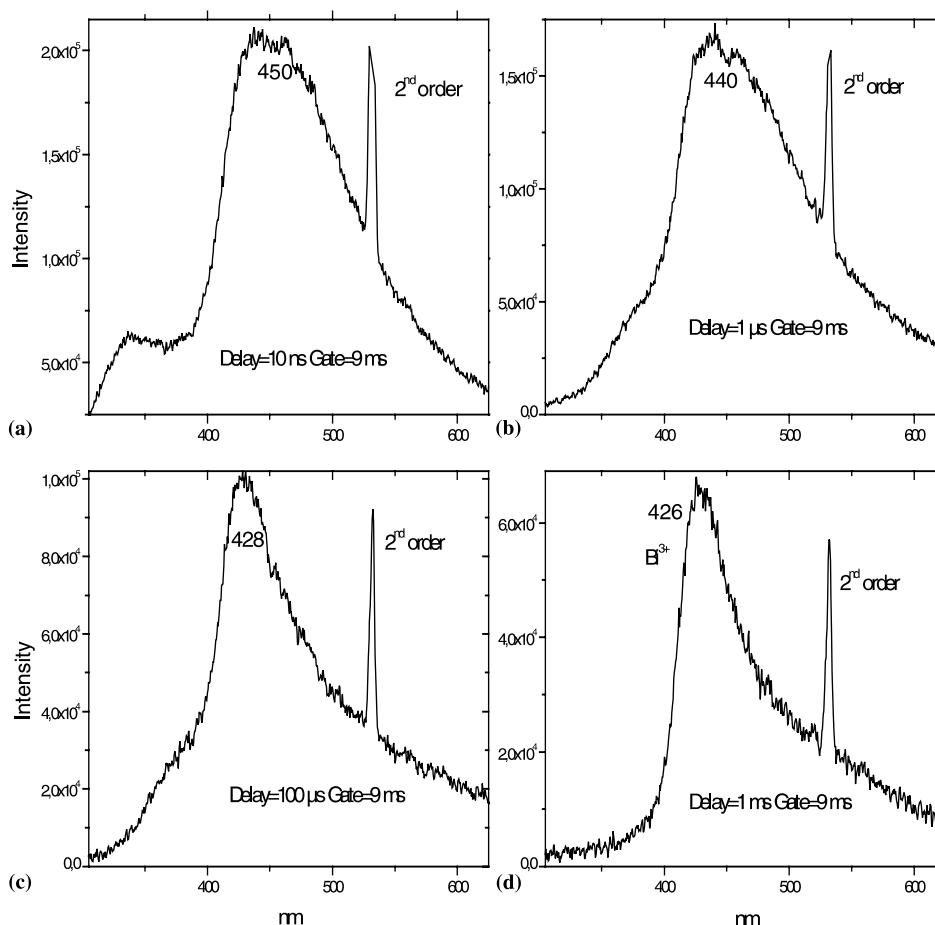


Fig. 10. Violet luminescence spectra of Bi^{3+} in mineral barite under $\lambda_{\text{ex}} = 266 \text{ nm}$.

100 ppm was also detected in [14]. Weak orange luminescence on the tail of the strong UV band was detected in $\text{BaSO}_4\text{:Ag}$ under X-ray excitation [15], while luminescence of Cu in barite was not studied. We investigated synthetic $\text{BaSO}_4\text{:Ag}$ and $\text{BaSO}_4\text{:Cu}$ by laser-induced time-resolved luminescence spectroscopy.

In $\text{BaSO}_4\text{:Ag}$ three bands are detected (Fig. 7): red, green and UV. The red one peaking at 650 nm at room temperature has half-width of 150 nm and decay time of 75 μs . The parameters are practically unchanged at lower temperatures, but the relative intensity is lower. The green band peaking at 500 nm has, at room temperature, a half-width of 80 nm and a decay time of 80 μs . At lower temperatures its relative intensity becomes stronger

and decay time shorter up to 20 μs at liquid helium. The UV band peaking at 375 nm at room temperature has a half-width of 45 nm and a decay time of 45 μs and its parameters are practically unchanged at lower temperatures. The spectrum of the first one is similar to broad orange band in natural barite (Fig. 1). Decay time of this band in artificially activated barite is shorter compared to the natural one, but it may be connected with much higher Ag content with resulting concentration quenching.

In $\text{BaSO}_4\text{:Cu}$ two bands are detected (Fig. 8): red and violet. The red one peaking at 740 nm at room temperature has half-width of 150 nm and decay time of 350 μs . The violet band peaking at 410 nm has at room temperature half-width of 35

nm and decay time of 7 μ s. At lower temperatures both bands disappears and the new IR one is detected. Such deep red luminescence in natural barite was not detected in present investigation. Nevertheless, it has been described earlier by one of the authors [2,3], while the possible connection with Cu was not considered. Now the exact origin of the band is established.

The possible luminescence centers may be Ag^+ and Cu^+ (d^{10} configuration). Complexes with monovalent d^{10} ions often show efficient luminescence at room temperature. The emission transition has been assigned to a d^9s – d^{10} transition, a ligand-to-metal charge-transfer transition, or a metal-to-ligand charge transfer transition, depending on the ligands [8,9]. For the sulfur ligands a ligand-metal character is proposed as evident [16]. As in the case of Bi^{3+} , the presence of several luminescence bands with strongly different decay times may be preliminary connected with excited state splitting [8] (Fig. 9).

Ag^+ is very big ion with ionic radius of 142 pm for coordination number 8, which is close to those of Ba^{2+} . It also can be proposed for Cu^+ substitution which is characterized by much more smaller ionic radius (91 pm) in the same approach that those of trivalent Bi^{3+} or rare earth ions.

3.4. Natural samples with violet–blue luminescence

As it was proved above, barite activation by Bi, Ag and Cu generates orange–red luminescence bands together with other emissions in the violet, blue and green parts of the spectrum. We studied natural barite luminescence in this spectral range also. The steady-state spectra are always very broad and not characteristic, but time-resolved spectroscopy enables us to separate several bands, which are very similar to those detected in artificially activated BaSO_4 . Fig. 10 represents luminescence spectra of natural barite composed of broad band peaking at 450 nm (Fig. 10(a)). After

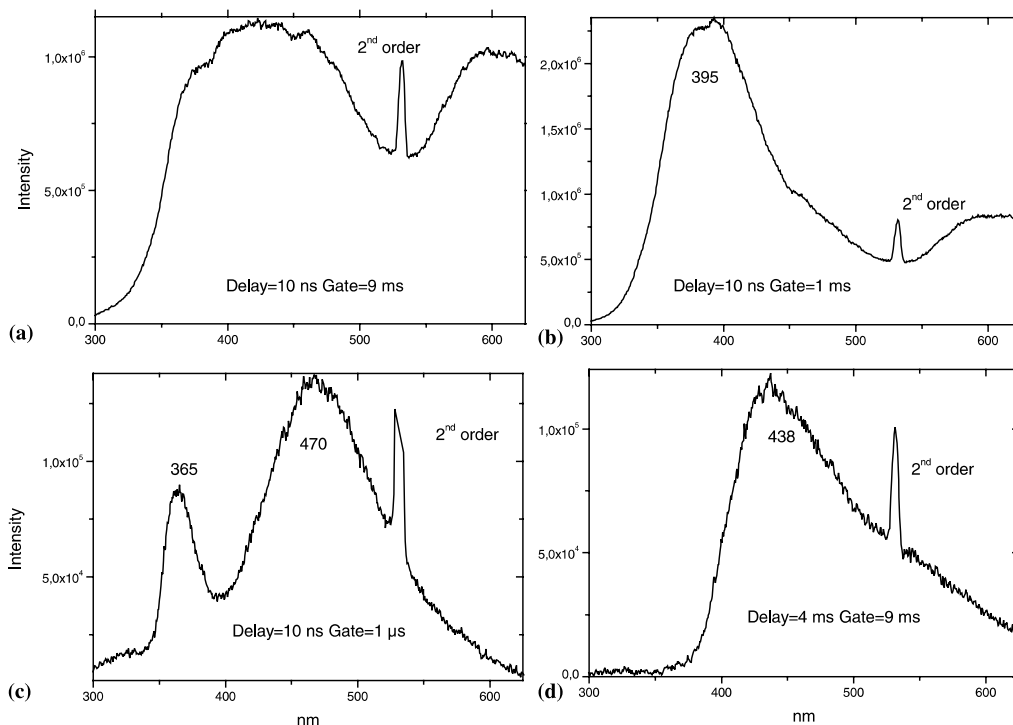


Fig. 11. Luminescence spectra of mineral barite heated at 600°C under $\lambda_{\text{ex}} = 266$ nm evidently connected with Ag^+ and Cu^+ centers.

long delay of 1 ms, when the emissions with long decay time are emphasized, the narrow violet band at 426 appears (Fig. 10(d)), which is absolutely similar to those ascribed to Bi^{3+} luminescence center. The same sample after heating in air at 600°C has different luminescence properties (Fig. 11). Intensive bands in the UV and blue–green appears with relatively short decay time, which are rather similar to the corresponding bands characteristic for Ag and Cu activation.

4. Conclusion

Natural barite BaSO_4 has very unusual luminescence properties for minerals. It is mainly connected with a very big Ba^{2+} ionic radius and its unusually higher coordination number of 12. Because of this, it is difficult to create luminescence centers usual for minerals, such as transition metal ions and rare-earth ions. Post-transitional elements such as Bi, Ag and Cu take part in blue, green and orange-red barite luminescence. They are well known centers in solid-state spectroscopy, but have not previously been considered in minerals.

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