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LUMINESCENCE OF Eu(III), Pr(III) AND Sm(III) IN CARBONATE-FLUOR-APATITE

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The purpose of this work was identification of luminescent lines occurring in natural carbonate-fluor-apatite (francolite) mineral. For identification of several rare earth ions occurring in natural francolite, the luminescence of rare earth ions was extensively studied in artificial mineral consisting of a pure francolite (not containing rare earth) of the composition $\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{O}):\text{Ca}_5(\text{PO}_4)_3\text{CO}_3$ activated with Pr, Eu and Sm ions and then compared with the luminescence features observed in natural mineral.

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1. Introduction

The mineral francolite (carbonate-fluor-apatite) $\text{Ca}_5(\text{PO}_4, \text{CO}_3)_3(\text{F}, \text{OH})$ occurs in vast deposits, and is utilized on a large scale allowing also the recovery of many by-products. The mineral is sometimes substantially enriched in rare earth elements making their extraction possible. The distinction between the various chemical forms of rare earth (RE) poses a fundamental problem. If they occur as an adsorbed or separate phase, selective extraction is possible. However, if they occur as structural substitute, they may be removed only by dissolving or melting the apatite host, thus requiring high energy uses [1].

The luminescence of the traces of RE ions have been studied extensively in natural and artificial fluorapatite $\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{OH})$. So far, no evidence from luminescence research exists about the exact location and valence of RE in francolite. It is the purpose of this work to examine the following questions: what is the valence of the RE present and where they are located.

2. Experimental

2.1. Samples

The sedimentary apatite in this study included approximately 100 samples from the phosphate of Israel and around the world (Russia, Estonia, USA, Jordan, Finland, Marocco, Albania). All samples were checked by infrared spectroscopy in order to exclude those with the impurities of foreign minerals (mainly calcite) which are able to serve as host matrix for luminescence centers.

2.2. Methods

To achieve our goals we have utilized the technique of time-delayed spectroscopy. This method permits spectral detection of elements having relatively weak luminescence with long decay times on the background of the strong emission of organic matter with extremely short decay (less than 20 ns).

The luminescence spectra were examined by UV laser excitation (308 nm) which delivers pulses of 10 nanoseconds duration and 0.1 cm^{-1} spectral width. The pulse energy was maintained at about 80 mJ. The luminescence observed at 90° was analyzed with a Hilger and Watt 1 monochromator with a grating of 1200 grooves/mm blazed at 500 nm. The luminescence in the range of 400–900 nm was detected by a fast response AsGa photomultiplier (RCA 31084) and the signal was fed into a Canberra multichannel analyzer for the lifetime data. The experimental setup was controlled by a PC computer. The lifetime analysis of the decay curves was accomplished with an Origin computer program which allows to achieve the best fit for experimental curve with several exponents and to assess their relative contributions.

Heating the samples up to 900°C causes significant changes in the luminescence. The thermal treatment was carried out in air, in the temperature interval of $300\text{--}900^\circ\text{C}$. The sample was held at each temperature for one hour and then cooled down to room temperature in the oven.

For the correct interpretation of the luminescent lines, artificial activation by different RE was accomplished by heating the mixtures of natural francolite with corresponding oxides (1% of Eu_2O_3 and 5% of Sm_2O_3 and Pr_2O_3) at 900°C in air. Artificial oxyapatite $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ was also activated at the same conditions.

3. Experimental results

Luminescence of RE is well known in natural fluorapatite [2, 3] but it was not detected in all natural carbonate–fluor–apatites under investigations. After heating the francolite samples in air at $800\text{--}900^\circ\text{C}$, a set of very intensive and narrow lines appears with the strongest maxima at 595, 619, 626, 634 and 646 nm (Fig. 1a). At liquid nitrogen temperature new lines appear at 603, 615, 651, 653 and 656 nm (Fig. 1b).

In order to distinguish some lines which belong to different sites, fluorescence decay was measured (Fig. 2). At room temperature the lifetimes of the 634 and 646 nm lines are practically the same with the main components of 0.023 and 0.7 ms. The line at 619 nm is characterized by much shorter decay time with

two main components of 0.002 and 0.09 ms. At nitrogen temperature the line at 650 nm has two main components of 0.07 and 0.09 ms. The other lines are weak and the measured values are uncertain.

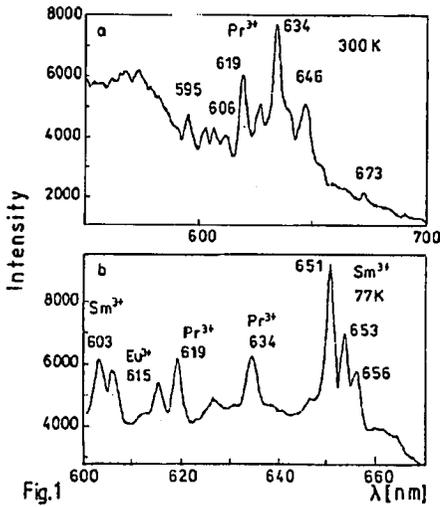


Fig.1

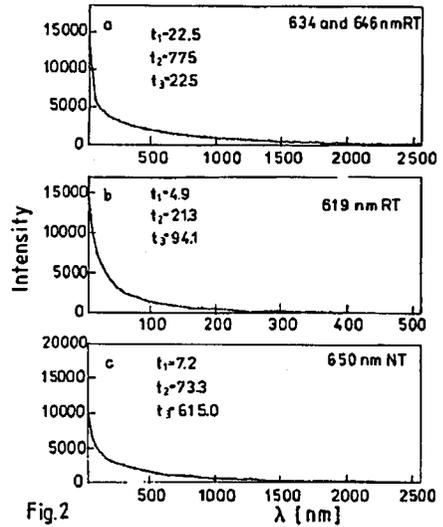


Fig.2

Fig. 1. Luminescence of RE in natural francolite after heating at 900°C.

Fig. 2. Fluorescence decay of different lines in carbonate-fluor-apatite.

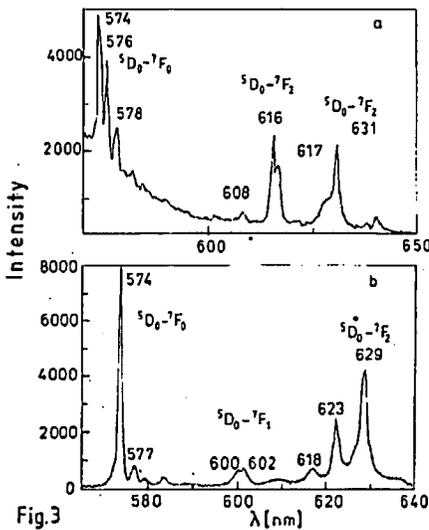


Fig.3

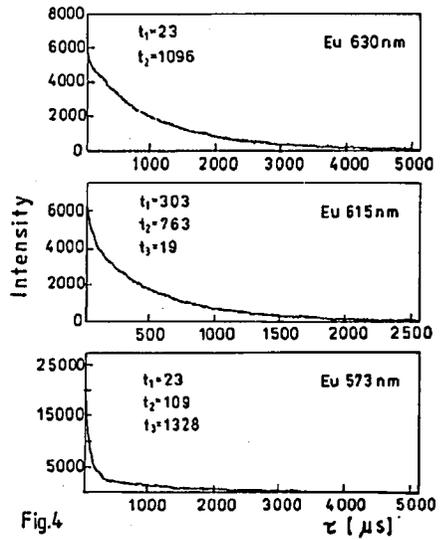


Fig.4

Fig. 3. Luminescence spectrum of Eu³⁺ in activated francolite (a) and oxyapatite (b)
 Fig. 4. Fluorescence decay of different lines in carbonate-fluor-apatite activated by Eu³⁺.

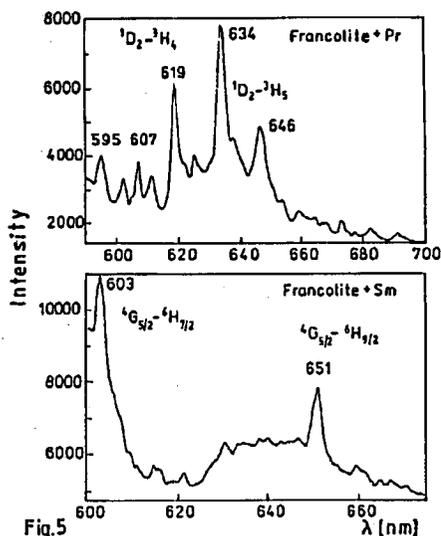


Fig.5

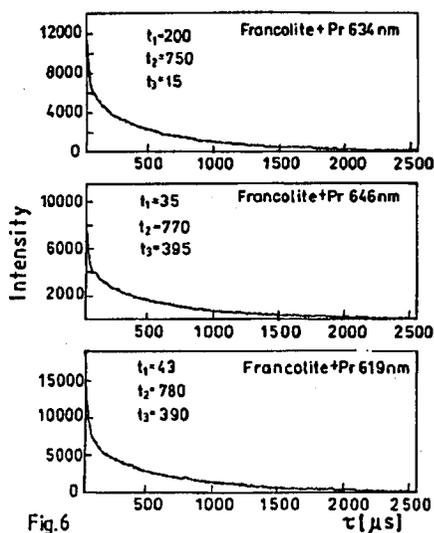


Fig.6

Fig. 5. Luminescence spectra of carbonate-fluor-apatite activated by Pr^{3+} and Sm^{3+} .
 Fig. 6. Fluorescence decay of different lines in the carbonate-fluor-apatite activated by Pr^{3+} .

In the luminescence spectrum of natural francolite activated by Eu^{3+} three groups of lines are observed (Fig. 3a). The first group has distinctive sharp lines at 574, 576 and 578 nm, while the second and the third groups are centered at 616 and 631 nm. In the luminescence spectrum of artificial oxyapatite activated by Eu^{3+} only two intensive groups are present at 575 and 630 nm, while the line at 617 nm is very weak (Fig. 3b). The lines at 574 nm and 630 nm in both cases have similar decay times of 1.1–1.3 ms (the short decay at 574 nm is connected with uranyl luminescence which is extremely strong in francolite after heating at 800°C [5]), while the line at 616 nm in francolite is characterized by shorter decay of 0.75 ms (Fig. 4).

Luminescence spectrum of natural francolite activated by Pr^{3+} consists of a number of groups of lines in the orange and red end of the spectrum (Fig. 5a). For the weak lines the values are uncertain, but for the strong ones the main decay components are rather similar (0.75–0.78 ms) (Fig. 6).

In luminescence spectrum of natural francolite activated by Sm^{3+} two groups of lines appear at 600 and 650 nm (Fig. 5b). The line at 650 nm has very strong long components of 2.8 ms, while such components are not detected for the line at 603 nm. These values are doubtful because of the strong background luminescence.

4. Discussion

4.1. Crystallochemical features

The composition of the ideal fluorapatite corresponds to formula $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$. There are 42 atoms in the unit cell and the parameters of fluo-

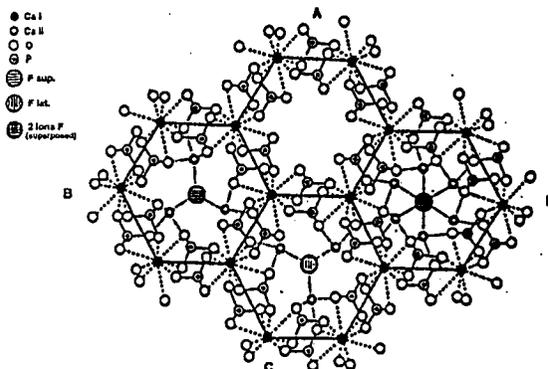


Fig. 7. The structure of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$.

roapatite are $a = 9.364 \text{ \AA}$, $c = 6.879 \text{ \AA}$. The structure of apatite is hexagonal with the symmetry group $P6_3/m$. There are three types of polyhedrons in the apatite structure: Ca(I), Ca(II) and PO_4^{2-} . Isolated orthophosphate groups are situated along the second order axes between the columns of Ca(I) and Ca(II). Isolated orthophosphate groups are situated in the center of the Ca(II) column along the hexagonal axis. There are two nonequivalent sites of the Ca^{2+} ions: 40% are associated with Ca(I) and 60% with Ca(II). The point symmetry of the Ca(I) site is C_3 with each Ca having six oxygen nearest neighbors which form a distorted triangular prism around the Ca^{2+} ion. The Ca(II) site has C_s symmetry with the Ca^{2+} ions sitting at the corners of equilateral triangles with F^- ion as the center (Fig. 7). The role of the carbonate ions in apatite is one of the most discussed problems in the crystallochemistry of apatite. It is proved by now that carbonate ions enter into the apatite structure and two nonequivalent positions were proposed: in place of the orthophosphate ions and on the hexagonal axis [2].

The presence of two cation sites suggests that upon activation with RE ions at least two types of activator centers can be formed. Moreover, because in such a heterovalent activation the need arises for excess charge compensation, which can be effected in different ways, the number of center types can even be larger.

4.2. Luminescence spectra of RE

4.2.1. Eu(III)

Trivalent europium ions are widely used as luminescent probes in the investigation of the crystallochemical structure of the activator centers. Particularly informative is the study of the transition between the two non-degenerate terms 7F_0 and 5D_0 . The presence of several lines in this region can be caused by the existence of several types of activator centers, while the relative intensity can serve as a characteristic of the local symmetry [6-12].

The luminescence of Eu^{3+} in carbonate-fluor-apatite has the following features:

1. The most intense lines near 575 nm may be unambiguously interpreted as a pure electronic transition ${}^5D_0 \rightarrow {}^7F_0$. Its strong relative intensity and unusually high position are similar to those detected in fluorapatite and oxyapatite [4, 13].

2. The ${}^5D_0 \rightarrow {}^7F_0$ region of the Eu^{3+} strong lines at 574, 576 and 578 nm suggests the multiplicity of activator sites which is more pronounced compared with oxyapatite activated by Eu^{3+} at the same conditions (Fig. 3). The ${}^5D_0 \rightarrow {}^7F_0$ transition is sufficiently large only in cases where the site symmetry allows an electric dipole process. The symmetries allowing such a process are C_s , C_v and C_{nv} [8]. Thus, it may be concluded that such centers are formed by replacement of low-symmetry Ca(II) sites with activator ions, while the different lines are connected with different ways of excessive charge compensation.

3. The lines at 631 nm have the similar decay time with the line at 574 nm (1.1 and 1.3 ms, correspondingly). It is possible to suppose that they belong to the same activator site and are connected with the ${}^5D_0 \rightarrow {}^6F_0$ transition.

4. The lines at 616 nm are much stronger compared to oxyapatite activated by Eu^{3+} at the same conditions (Fig. 3). Their spectral position is also typical of ${}^5D_0 \rightarrow {}^6F_0$ transition. The large magnitude of this hypersensitive transition and the shorter decay time of 0.75 ms indicate that we deal with another activator site with larger asymmetric part of the crystal field. The relocation of carbonate ions during heating from the position of orthophosphate groups of the hexagonal axes may be responsible for the symmetry lowering of the Ca(II) position [2].

4.2.2. Pr(III)

The luminescence of Pr^{3+} in carbonate-fluor-apatite has the following features:

1. The blue luminescence which is connected with ${}^4P_0 \rightarrow {}^3H_4$ transition and is very intensive in fluorapatite [4] is not detected.

2. Two sequences of lines may be detected: 595, 607, 619, 634 nm and 602, 611, 625 and 646 nm. It is possible to suppose that they represent two activator sites with slightly different symmetries. The similar decay times of the lines indicate that the corresponding transitions are connected with the same excited level 3P_0 or 1D_2 . A detailed study of this topic will be presented later, but the relatively long decay time is in the favor of the 1D_2 level [14]. The luminescence quenching from the 3P_0 level in the carbonate-fluor-apatite may be due to a transfer of excitation energy to the vibrations of the lattice. For RE when considerable quenching occurs the energy difference between the electronic levels approximately equals the energy of four phonons [15]. The energy difference between the 3P_0 and the lower 1D_2 levels is approximately 3580 cm^{-1} which is practically equal to the four phonons of the ν_2 vibration of the carbonate groups ($870\text{--}880 \text{ cm}^{-1}$ [2]).

4.2.3. Sm(III)

The luminescence of Sm^{3+} in carbonate-fluor-apatite is very similar to those in fluorapatite [4] with two distinct lines connected with ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$ (603 nm) transitions. The possible reason is that the radiating term is separated from the nearest lower level ${}^7F_{11/2}$ by an energy interval of 7500 cm^{-1} which is too large

compared to the energy of phonons of carbonate groups to accomplish an effective nonradiative relaxation of excited levels.

It is interesting to note that Sm³⁺ luminescence in fluorapatite activated in the reduced conditions is different [1]. The possible reason is the formation of the centers by replacement of low-symmetry and high-symmetry calcium sites, but this problem needs further clarification.

4.3. Natural luminescence

The experiments with artificial activation of carbonate-fluor-apatite allow to interpret the luminescence lines found in natural samples. According to their spectral position, the lines at 603, 651, 653 and 656 nm may be ascribed to Sm³⁺, the lines at 606, 619 and 646 nm to the Pr³⁺, the line at 615 nm to Eu³⁺ and the line at 634 nm is connected with Pr³⁺ and Eu³⁺ ions.

Decay times of the lines at 634 and 646 nm in natural samples and activated by Pr³⁺ are also close (0.7–0.78 ms) which confirms their connection. The decay time of the line at 619 nm is much shorter in natural sample in comparison with activated one. This problem needs further investigation.

Luminescence of RE is well known in natural fluorapatite [1, 16] but in carbonate-fluor-apatite it is observed only after heating. Two possibilities exist to explain this difference. It is possible that in carbonate-fluor-apatite the luminescence is quenched by the components with high-energy phonons. The latter may be represented by water and organic matter which are present in carbonate-fluor-apatite in much larger quantities as compared to fluorapatite. They are removed after heating and luminescence becomes visible. Another possibility is that carbonate-fluor-apatite accommodates RE in concentrated adsorbed form, which quenches the fluorescence by concentration interaction [3, 15]. As a result of high temperature heating, thermal diffusion of RE in lattice takes place with resulting luminescence.

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