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Luminescence of uranium in natural apatites

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Abstract

In sedimentary apatite two types of uranyl were observed, sorption of uranyl aquecomplexes and films of uranyl minerals. Tetravalent uranium is detected by the weak reabsorption lines. Hexavalent uranium was detected after oxidizing thermal treatment at 1100 K, as concentrated in fluorite phase which is formed as result of heating. Uranyl luminescence is absent in magmatic apatites before and after oxidizing heating, indicating that the main form is due to tetravalent uranium. © 1998 Elsevier Science S.A.

Keywords: Apatite; Uranium; Luminescence

1. Introduction

Magmatic fluor-apatite $Ca_5(PO_4)_3F$ is characterized by a bright luminescence with different spectral-kinetic properties. As result of its detailed study under X-ray, UV lamp and laser excitations the luminescence of REE^{2+} (Eu, Sm, Yb), REE^{3+} (Ce, Tb, Tm, Dy, Er, Sm, Pr, Eu, Yb, Nd), Mn^{2+} and Mn^{5+} have been established [1–3]. Sedimentary carbonate-fluor-apatite $Ca_5(PO_4,CO_3)_3F$ is not luminescent under X-rays, and under UV lamp excitation it is characterized by broad structureless bands which are very similar to those encountered in many sedimentary minerals. It was concluded that this luminescence is due to different kinds of water–organic complexes [3]. For this reason the luminescence properties of the sedimentary apatites is much less informative and has not attracted much attention. It was noted that in phosphorite from the Santa Margarita Formation, California, luminescence intensity in the visible region correlates with uranium and cadmium contents [4].

Carbonate-fluor-apatite accommodates large quantities of trace elements, mainly uranium, which are potential luminescence centers. It has been proposed that uranium may occur in phosphorites in the following forms: as a separate uraninite phase; as an adsorbed or structurally incorporated uranyl ion; as dominantly a U^{4+} replacement for Ca^{2+}; to be structurally incorporated appreciably as both U^{4+} and U^{6+} [5].

The distinction of the various forms of occurrence is fundamental and at the same time controversial problem. In many cases luminescence of minerals helps not only to identify an element, but also to determine its valence unambiguously and also features specific for its position in a structure [6].

The steady-state luminescence of water–organic comlexes is strong and conceals the weaker characteristic luminescence of uranium-containing centers, which can be detected by the difference in decay times only. The reason is that the decay time of water–organic complexes is characterized by two time intervals: less than 30 ns and more than 10 ms. Since the uranium centers have decay times in the microseconds range, it is possible to detect them by time-resolved spectroscopy. In time-delayed laser-induced spectroscopy, the luminescence spectra are recorded at a fixed moment after a laser pulse. These spectra may be different from the integrated steady-state ones since, after a certain time, short luminescence will be practically absent.

Thermal treatment has great influence on luminescence spectra. Certain cations may change valence and accommodation form during heating, with transformation from nonluminescent form to luminescent [7].

The aim of this work is the systematic study of sedimentary apatite luminescence using a time-resolved laser-induced method combined with a step-like thermal treatment. Such a method, for example, allowed to estab-

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lish the luminescence of Pr^{3+}, Sm^{3+}, Eu^{3+} and Mn^{5+} which were absorbed by the sedimentary apatite surface and that the structural incorporation was the result of thermal diffusion [2,8].

2. Experimental

Excitation has been obtained at 308 nm with a XeCl eximer laser (Lumonix 520) which delivers pulses of 10 ns duration and 0.1 cm^{-1} spectral width. The pulse energy has been maintained to about 80 mJ. The luminescence observed at 90° was analyzed with a Hilger and Watt 1-m monochromator with a grating of 1200 grooves mm^{-1} 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. For the short (less then 1 μs) fluorescence spectroscopy the signal was fed into SR250 Boxcar and digitized, while decay time was measured by Lecroy 9410 digital oscilloscope. The experimental set-up was controlled by a PC computer. All samples were investigated at room (300 K) and liquid nitrogen (77 K) temperatures. The emission spectra are corrected from the spectral response of the apparatus.

The lifetime analysis of the decay curves was accomplished with an ORIGIN computer program which allows to achieve the best fit for the experimental curve by several exponents and to assess their relative contributions.

The thermal treatment was carried out in air, in the temperature interval of 300–900°C, in steps of about 100°C. The sample was held for 1 h at each temperature and then cooled down to room temperature in the oven.

The collection of sedimentary apatites under investigation includes approximately 100 samples mainly from Israel, but also from all around the world (Russia, Estonia, USA, Jordan, Finland, Morocco, Albania). All samples were checked by micro-Raman and IR spectroscopy in order to exclude those with impurities of foreign minerals which are able to serve as host matrix for U (mainly calcite).

3. Results

Spectra of the laser-induced luminescence of apatites with long decay times (more then 1 μs) consist of several sets of relatively narrow bands in the green part of the spectrum which are characterized by the clear vibrational structure. The first type contains, at 300 K, the characteristic set of maxima at 484, 504, 526, and 546 nm. At 77 K the intensity only slightly increases, the spectrum is nearly the same, but the structure is more pronounced (Fig. 1a). The luminescent decay measured at 526 and 504 nm may be represented by the exponential fitting with the main decay component of 350 μs. The second type contains, at 300 K, the set of bands at 467, 486, 505, 526 and 547 nm (Fig. 1b). At 77 K the intensity is much stronger, the band at 467 nm disappears and the other bands are narrower. The quenching of the emission monitored at 526 nm at 300 K may be represented by the exponential fitting with the main decay component of 200 μs. The third type contains, at 300 K, the bands at 508 and 524 nm which are the strongest at 77 K (Fig. 1c). The quenching of the emission monitored at 524 nm at 300 K may be represented by the exponential fitting with the main decay component of 300 μs.

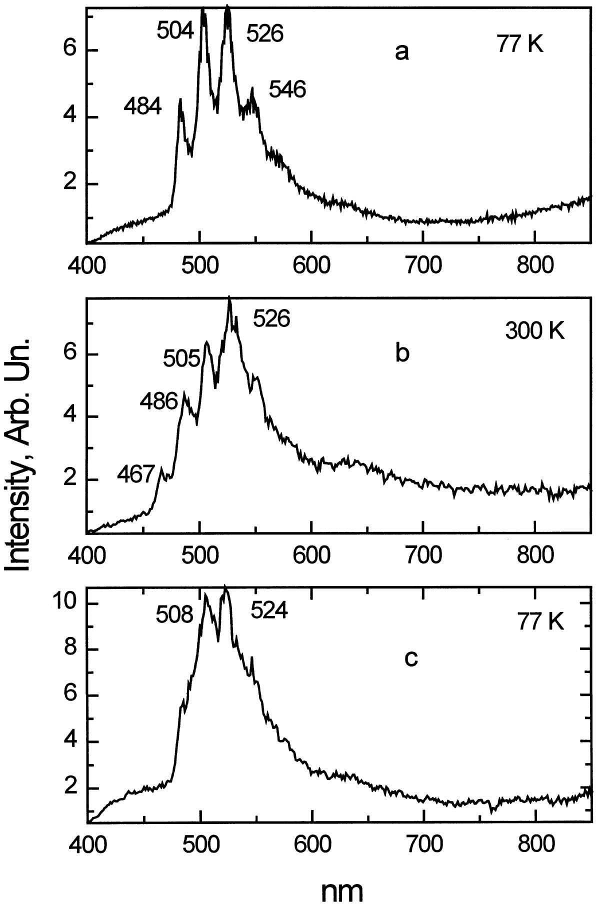

Fig. 1. Laser-induced long-lived (more than 1 μs) luminescence of uranyl adsorbed on sedimentary apatite surface: secondary uranyl minerals, probably andersonite and liebigit (a,b), and uranyl aquacomplexes (c).

The laser-induced time-delayed luminescence spectra of many sedimentary apatites contain several ‘negative’ lines at the red part of the visible spectrum (Fig. 2). The correlation analyses reveal that this group is subdivided into three: the strongest line at 760 nm accompanied by the weaker line at 687 nm; doublet at 720 nm accompanied by triplet at 823 nm; the line at 656 accompanied by the lines at 575 and 615 nm.

The following results allow us to conclude that these lines are not related to noise or artifacts: the spectral features are ‘negative’, thus they may not be connected with second-order lines or an incidental source of light; the spectrum is presented without any smoothing or other

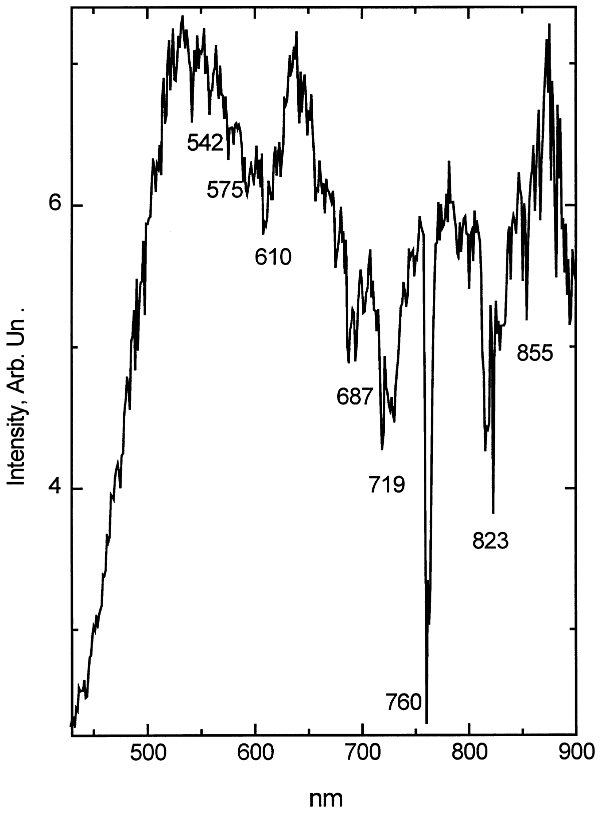

Fig. 2. Reabsorbtion in the laser-induced long-lived (more than 1 μs) luminescence spectrum of apatite: tetravalent uranium U^{4+} (575, 615 and 656 nm), molecular oxygen O_2 (687, 760 and 763 nm) and molecular water H_2O (719 and 855 nm).

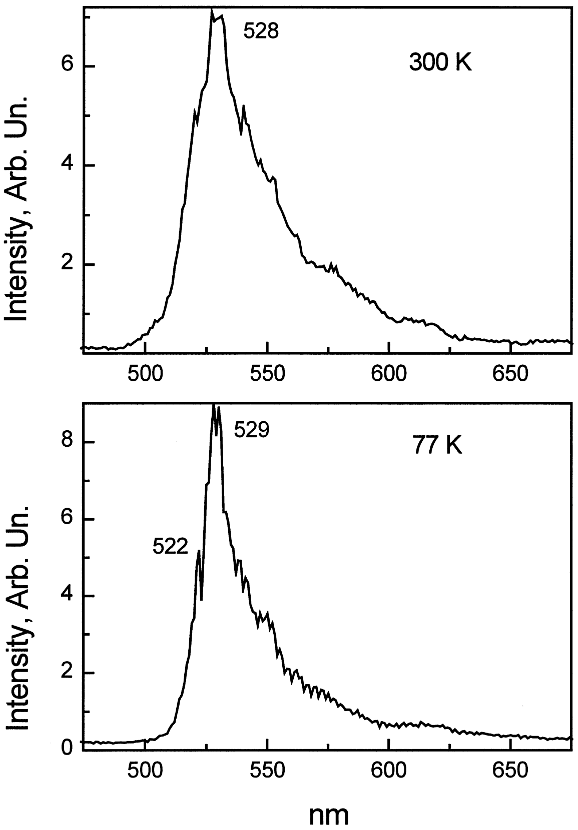

Fig. 3. Laser-induced long-lived (more than 1 μs) luminescence of hexavalent uranium U^{6+} after oxidizing thermal treatment at 1100 K as concentrated in fluorite which is formed as result of heating.

mathematical treatment and it is clearly seen that negative lines are much stronger then the noise. Besides that, the negative lines are always situated at the same places. The invariability of the spectral positions provides the evidence that they are not connected with laser and detection system fluctuations.

It is known that luminescent properties under UV lamp excitation of the sedimentary phosphorites are strongly changed after oxidizing thermal treatment [7]. Thermal annealing at temperatures of up to 600°C did not cause spectral changes, but above that temperature drastic alteration took place. The spectra at 300 K are characterized by a very strong structureless band with maximum at 527 nm (Fig. 3a). The decay curve has the main component of ~110 μs. At 77 K the spectrum is strongly changed with the intensive narrow line at 521 nm (Fig. 3b). The decay is substantially slower with the main component of ~280 μs.

4. Discussion

It is well known that certain minerals, which contain uranium as the uranyl ion, UO_2^{2+}, exhibit fluorescence with distinctive spectral and temporal characteristics. The photoluminescence of nearly 40 uranyl minerals was investigated at 300 and 77 K, mainly under UV lamps, but also under UV laser excitation [3,9,10]. The origin of the excitation and emission bands of UO_2^{2+} is the charge transfer between the molecular orbitals of oxygen and the 5f orbitals of uranium [11]. A feature distinguishing the molecular excitation and luminescence spectra of UO_2^{2+} is the fact that they arise from the transitions between electron-vibrational levels, i.e. the levels of electronic states split into sublevels whose spacing equals the vibrational frequency of the molecule [6]. The color of luminescence of uranyl in different minerals changes from a green-blue to the orange-red, and the mean frequency interval alters from 840–880 to 680 cm^{-1}, correspondingly. The UO_2^{2+} always exhibits comparably long decay times in the range of 60–600 μs. Some of them fluoresce strongly at 300 K, some relatively weakly and others do not fluoresce at all. The emission of some of the weakly fluorescent uranyl minerals is dramatically increased by cooling to 77 K. The differences in the luminescence parameters are connected with the energy migration probability between the uranyls which, in turn, depends on the mineral structure, the connection type between various uranyl units, and the chemical nature of ligands which interact with uranyl [10].

The spectral-kinetic parameters of the green laser-induced luminescence of the sedimentary apatites allow its association with UO_2^{2+} emission. The spectra presented in

Fig. 1a,b are typical for uranyl minerals and it is possible to suppose that we are dealing with a separate uranyl mineral phase on the apatite surface. Comparison with the known laser-induced luminescence of other uranyl minerals shows that those with the most similar spectral-kinetic parameters are andersonite $Na_2Ca(UO_2)(CO_3)_3 \times 6H_2O$ and liebigite $Na_2(UO_2)(CO_3)_3 \times 10H_2O$ [9], but this identification is ambiguous.

The highly fluorescent uranyl ion may also be present in other geological materials, such as siliceous matrices, calcites and barites [3,8–10]. This luminescence is effectively excited only by the short UV and its decay time is in the range of several hundreds of μs. Three different models of uranyl ion interrelation with host mineral were proposed: surface films of uranyl-containing minerals; presence in the host matrices that are relatively transparent at the excitation and luminescence wavelength of UO_2^{2+}; physical sorption of uranyl aquecomplexes.

The spectra of the green laser-induced luminescence represented in Fig. 1c, together with their decay time, also allows its association with UO_2^{2+}. These luminescence spectra strongly differ from the spectral parameters of the all known uranyl minerals. For this reason this type of green luminescence is not possible to connect with finely dissipated uranyl phases. On the other hand, this luminescence is very similar in such different host minerals as sedimentary apatites, opalites, chalcedony, chert, quartz and barites. Luminescence independence from the mineral's structure evidences that it may be connected with uranyl adsorption on the mineral's surface, supposedly in the form of $(UO_2 \times nH_2O)^{2+}$.

The negative lines can be attributed to the reabsorption of the broad luminescence band with a long decay time of 5–6 ms. The lines in the spectral range from 687 to 830 nm belong to molecular oxygen and water [12]. The lines at 575, 615 and 656 nm are not connected with them and are due to another cause. They are very similar to the reabsorption lines of U^{4+} in zircon [7] and may be tentatively ascribed to this center.

When the samples are heated the emission spectra (Fig. 3a) are much less structured, more intensive and short-lived. It is known [13] that uranyl, which is a linear triatomic molecule, can form complexes with ligands in the equatorial plane. When OH group or F are the complexing species, the bond is very weak, since there is no significant overlap of the molecular orbital of the ligands with those of the uranyl. As result, a well-resolved spectrum is obtained, resembling gaseous molecules, resulting from the electron transitions from the oxygen to the 5f orbitals of the uranium. The spectra become much less resolved with stronger ligands occupying the equatorial plane. When water molecules are evolved at elevated temperatures, the OH groups disappear and, probably, P ligands become strongly bonded with uranyl orbitals in the equatorial plane. The spectrum becomes less distinct, the intensity increases because of the less-pronounced presence of a center of inversion which makes the parity-forbidden transitions in uranyl more allowed and, correspondingly, this is followed by shortening of the decay time.

Spectral parameters of the structured green luminescence (Fig. 3b) are absolutely similar to those of U^{6+} luminescence in fluorite after thermal treatment [3]. It is known that during the calcination of the sedimentary phosphates new mineralogical phases, including fluorite, are formed [14]. Taking these data into account, it is possible to conclude that, after thermal treatment, uranium is concentrated in fluorite lattice in the form of U^{6+}.

It is interesting to note that in magmatic apatites the luminescence of uranium-containing centers have not been discovered as before and after oxidizing heating. Thus, it is reasonable to suppose that uranium is present mainly in U^{4+} form, which has been established by the EPR method [15]. The U^{4+} with an ionic radius of 0.97 Å may be located in the apatite structure instead of Ca^{2+} with an ionic radius of 0.99 Å. The most possible way for excess charge compensation is Na^+ for Ca^{2+} structural substitutions. The absence of U^{4+} reabsorption may be connected with lower uranium concentration compared to sedimentary apatites.

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