

Distribution and luminescence characteristics of Ce^{3+} ions in calcium hydroxyapatite

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The luminescence characteristics of Ce^{3+} ions in calcium hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ have been studied under excitation within the 3.5–15 eV region. It has been found that in $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ prepared in a reducing atmosphere, Ce^{3+} ions tend to occupy preferably high symmetry Ca(I) sites. The energies of all 5d crystal field levels of Ce^{3+} ions in Ca(I) sites have been determined. In addition to the 4f→5d excitation bands, the excitation spectrum of the Ce^{3+} emission shows a band with a maximum at 7.7 eV which is attributed to the host lattice absorption. The influence of the structural features of $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ on the luminescent behavior of Ce^{3+} is discussed.

Изучены люминесцентные свойства ионов Ce^{3+} в гидроксипатите кальция $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ при возбуждении в области 3,5–15 эВ. Установлено, что в $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, полученном в восстановительной среде, ионы Ce^{3+} проявляют тенденцию занимать высокосимметричные Ca(I)-позиции. Определены энергии всех компонентов 5d-конфигурации ионов Ce^{3+} в позициях Ca(I). В спектре возбуждения люминесценции ионов Ce^{3+} , помимо полос 4f→5d, также наблюдается полоса с максимумом 7,7 эВ, которая обусловлена собственным поглощением гидроксипатита кальция. Обсуждается влияние структурных особенностей $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ на люминесцентные свойства ионов Ce^{3+} .

Compounds and solid solutions with the apatite type structure are of great interest since those can be used as luminescent materials, catalysts, and ion exchangers. In recent years, calcium hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, has gained special attention due to its possible applications as a biomaterial [1, 2]. This compound belongs to the hexagonal system with the $P6_3/m$ space group. In this lattice, two nonequivalent calcium sites are present: Ca(I) with C_3 symmetry is surrounded by nine oxygen atoms, and Ca(II) with C_S symmetry is coordinated to six oxygen atoms and one OH⁻ group [3–5]. It is believed that the disordering of OH⁻ ions in c-axis columns causes a structural complexity of $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$.

It is well known that apatites can accommodate a large number of different ions in their lattice. The distribution of trivalent lanthanides (Ln^{3+}) between the two alkaline earth sites in different apatites has been the subject of numerous studies [4, 6–10]. It has been found that trivalent lanthanides at Ca(II) position are characterized by abnormally high values of Stark splitting. This provided a distinction of the spectral features of these ions from those of Ln^{3+} in Ca(I) position. However, the results obtained are contradictory. For example, the luminescence properties of Eu^{3+} in calcium apatites under UV excitation have been studied by several authors [6, 10]. Those authors have concluded that Eu^{3+} ions oc-

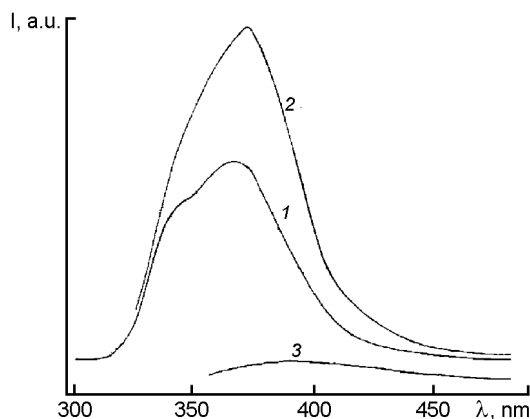


Fig. 1. Emission spectra of $\text{Ca}_{10(1-x)}\text{Ce}_{10x}(\text{PO}_4)_6(\text{OH})_2$ ($x = 0.005$) at 293 K under excitation at $\lambda_{exc} = 248$ nm (1); $\lambda_{exc} = 318$ nm (2); $\lambda_{exc} = 350$ nm (3).

copy mainly the Ca(II) positions. In contrast to this conclusion, Karbowski and Hubert [9] have reported that the nature of site occupancy by Eu^{3+} in calcium fluoroapatite varies depending on the material preparation method.

As far as we know, no reports on the luminescence properties of Ce^{3+} ions in synthetic calcium hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ have appear to date. It is well known that Ce^{3+} ion shows allowed the $4f-5d$ type optical transitions in absorption and emission. The emission band has usually a doublet structure which is due to the spin orbit splitting of the $4f1$ ground state into two components $2F5/2$ and $2F7/2$ with a separation of about 2000 cm^{-1} . In this paper, we report on the luminescence of Ce^{3+} ions in $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ under excitation in the 3.5–15 eV region. A comparison with the luminescence characteristics of Ce^{3+} ions in $\text{Ca}_2\text{B}_5\text{O}_9\text{Cl}$ [11] and CaBPO_5 [12] is also made.

Two samples of general formula $\text{Ca}_{10(1-x)}\text{Ce}_{10x}(\text{PO}_4)_6(\text{OH})_2$ ($x = 0.0001; 0.005$) were used for luminescence measurements. Both samples were prepared by solid state reactions. Stoichiometric amounts of CaCO_3 , $(\text{NH}_4)_2\text{HPO}_4$ and Ce_2O_3 with the atomic ratio $(\text{Ce}+\text{Ca})/\text{P} = 1.667$ were mixed and calcined at 300°C for 3 h and then at 800°C for 3 h in air. The samples were cooled, mortared to ensure homogeneity and calcined again at 1100°C for 8 h in a reducing atmosphere (CO). The samples were checked by X-ray diffraction (XRD) using Cu K_α radiation. No impurity phases were detected in the XRD patterns. The emission

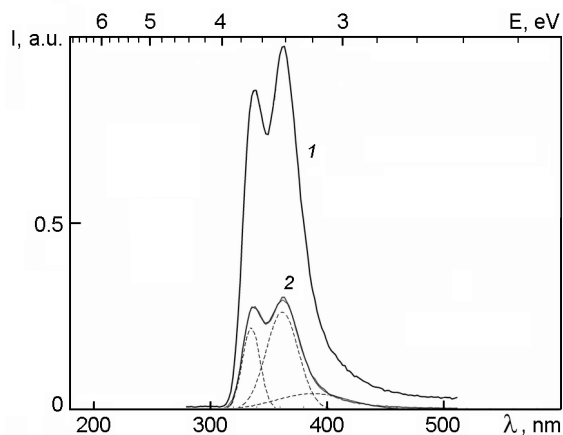


Fig. 2. Time-resolved emission spectra of $\text{Ca}_{10(1-x)}\text{Ce}_{10x}(\text{PO}_4)_6(\text{OH})_2$ ($x = 0.005$) at 8 K under excitation at $\lambda_{exc} = 266$ nm. The spectra were recorded for two different time intervals (Δt) after picosecond pulse excitation: $\Delta t = 1-190$ ns (1); $\Delta t = 1-8$ ns (2). The curve (2) was fitted by Gaussian-type bands (dotted lines).

and excitation spectra were recorded at room temperature using a LOMO SDL 1 spectrofluorimeter equipped with a xenon lamp. The spectra were corrected for the photomultiplier sensitivity and the monochromator efficiency using a calibrated light source. The measurements of excitation spectra at wavelengths shorter than 230 nm and the decay time measurements were performed at 8 and 293 K using synchrotron radiation and the equipment of the SUPERLUMI experimental station [13] of HASYLAB (Hamburg, Germany). The vacuum ultraviolet excitation spectra were corrected for the wavelength-dependent excitation intensity with using sodium salicylate as a standard. Since the luminescence properties of samples with $x = 0.0001$ and 0.005 were found to be the same, we will report only those for $x = 0.005$ sample.

The emission of the $\text{Ca}_{10(1-x)}\text{Ce}_{10x}(\text{PO}_4)_6(\text{OH})_2$ solid solutions depends on the excitation wavelength. The emission spectra of $\text{Ca}_{10(1-x)}\text{Ce}_{10x}(\text{PO}_4)_6(\text{OH})_2$ ($x = 0.005$) at 293 K for three different excitation wavelengths are presented in Fig. 1. Under excitation in the 240–300 nm region, the emission (curve 1) extends from 310 to 430 nm. It has two maxima at ~338 and 364 nm. The spectrum under excitation at $\lambda_{exc} = 318$ nm (curve 2) consists of a broad band with a maximum at 375 nm, whereas excitation at $\lambda_{exc} = 350$ nm produces the spectrum (curve 3) where a weak and

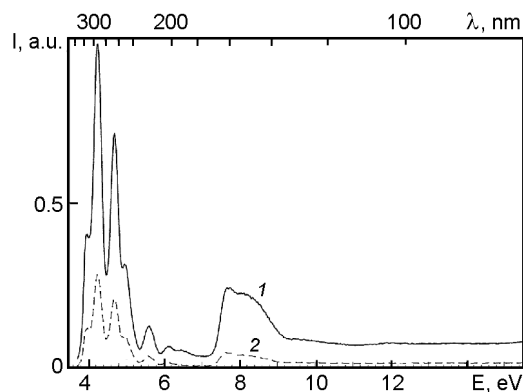


Fig. 3. Time-resolved excitation spectra for the emission of $\text{Ca}_{10(1-x)}\text{Ce}_{10x}(\text{PO}_4)_6(\text{OH})_2$ ($x = 0.005$) at 360 nm at 8 K. The spectra were recorded for two different time intervals (Δt) after picosecond pulse excitation: $\Delta t = 1-190$ ns (1); $\Delta t = 1-8$ ns (2).

structureless band with a maximum at about 395 nm dominates. It is evident that various kinds of centers involving Ce^{3+} are formed in $\text{Ca}_{10(1-x)}\text{Ce}_{10x}(\text{PO}_4)_6(\text{OH})_2$ ($x \leq 0.005$) solid solutions. Since the spectra of different centers show a considerable overlap, the luminescence measurements have been also performed at low temperature. Fig. 2 shows the time-resolved emission spectra of the $\text{Ca}_{10(1-x)}\text{Ce}_{10x}(\text{PO}_4)_6(\text{OH})_2$ ($x = 0.005$) at 8 K upon excitation at $\lambda_{exc} = 266$ nm. These spectra are similar to that shown in Fig. 1 (curve 1). Both spectra can be reasonably decomposed into three Gaussian-type bands peaked at 335, 362 and 388 nm. It is evident that the maxima at 335, 362 nm are due to transitions from the lowest Ce^{3+} $5d$ excited state to the $4f$ ground state levels ${}^2F_{5/2}$ and ${}^2F_{7/2}$. The energy gap between the maxima (1960 cm^{-1}) coincides with the spin-orbit splitting of Ce^{3+} ground state. We will denote all the centers related to the 338 and 362 nm emission bands as Ce_I . It is clear that the spectra in Fig. 2 are mainly due to the Ce_I emission. The centers related to the 395 nm emission band (Fig. 1, curve 3) will be denoted as Ce_{II} . Note that the Ce_{II} emission band does not show its characteristic doublet structure, indicating that there are several Ce^{3+} centers with overlapping spectra. In order to determine the nature of Ce^{3+} centers responsible for the emission of $\text{Ca}_{10(1-x)}\text{Ce}_{10x}(\text{PO}_4)_6(\text{OH})_2$ ($x = 0.005$), this sample was subjected to additional annealing at 1100°C for 3 h in air. No significant change either in the emission spectrum structure or the emission

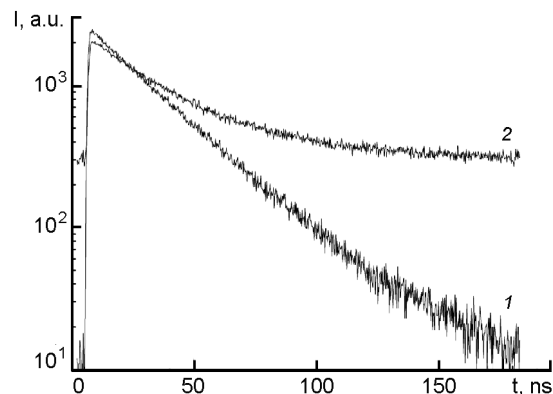


Fig. 4. Decay curves of the emission at 360 nm of $\text{Ca}_{10(1-x)}\text{Ce}_{10x}(\text{PO}_4)_6(\text{OH})_2$ ($x = 0.005$) at 8 K recorded upon excitation $\lambda_{exc} = 266$ nm (1); $\lambda_{exc} = 160$ nm (2).

intensity was observed. This indicates that the Ce_I centers are quite stable.

The time-resolved excitation spectra of $\text{Ca}_{10(1-x)}\text{Ce}_{10x}(\text{PO}_4)_6(\text{OH})_2$ ($x = 0.005$) for the emission at 360 nm at 8 K are shown in Fig. 3. The short-time excitation spectrum (curve 2) consists of several bands at 313, 291, 265, 249, 221, and 201 nm. It is evident that these bands are due to direct excitation of the Ce^{3+} ions via transitions to the components of Ce^{3+} $5d$ configuration. Also, there is a sharp emission intensity increase between 7.4 and 7.7 eV. The local maximum at ~ 7.70 eV (161 nm) can be assigned to a band gap transition followed by energy transfer to Ce^{3+} ions. Between 10 and 15 eV, the emission intensity does not change with increasing excitation energy. The time-integrated excitation spectrum (curve 1) has the same structure. The six Ce^{3+} $4f \rightarrow 5d$ bands at 313, 291, 265, 249, 221, and 201 nm are well observable. It should be noted that, in contrast to other bands, the excitation around 313 nm produces the spectrum with an emission maximum at about 375 nm (see Fig. 1, curve 2). Thus, the lowest excitation band of the Ce_I emission is situated at 291 nm, so that the Stokes shift of this emission amounts 4200 cm^{-1} . The excitation band at 313 nm should be attributed to other Ce^{3+} centers emitting at longer wavelengths. Their possible origin will be discussed below.

The decay curves of the of $\text{Ca}_{10(1-x)}\text{Ce}_{10x}(\text{PO}_4)_6(\text{OH})_2$ ($x = 0.005$) emission at 8 K for two different excitation wavelengths are presented in Fig. 4. Under excitation at $\lambda_{exc} = 266$ nm, the decay is nearly exponential and it can be charac-

terized by a time constant (τ) of 27 ± 1 ns. This value is typical of $\text{Ce}^{3+} 5d \rightarrow 4f$ transitions. The same result was obtained under excitation of the Ce^{3+} emission in any of the $4f \rightarrow 5d$ bands. At excitation at $\lambda_{exc} = 160$ nm (7.65 eV), the decay (Fig. 4, curve 2) shows a strong deviation from exponential behavior. Also, a slow component with a $\tau > 10^{-6}$ s is present. This indicates that the excitation of cerium ions is caused by sequential hole and electron captures.

Thus, several types of Ce^{3+} centers are formed in $\text{Ca}_{10(1-x)}\text{Ce}_{10x}(\text{PO}_4)_6(\text{OH})_2$ ($x \leq 0.005$) solid solutions. To determine the nature of the dominant Ce_I centers, we have compared their luminescence characteristics with those of Ce^{3+} ions in $\text{Ca}_2\text{B}_5\text{O}_9\text{Cl}$ and CaBPO_5 . It should be noted that Ce^{3+} ions in these compounds substitute for calcium ions and are in nine-fold coordination. However, in CaBPO_5 , the calcium ions are surrounded by oxygen ions only, whereas in $\text{Ca}_2\text{B}_5\text{O}_9\text{Cl}$, they are surrounded by seven oxygen ions and two halogen ions. It is known that the depression in energy position of the lowest $5d$ level of Ce^{3+} ion in a crystal can be considered as a result of two independent contributions, namely the centroid shift E_c , defined as the energy shift of the $\text{Ce}^{3+} 5d$ configuration barycenter relative to the free ion value (51225 cm^{-1}), and the total crystal field splitting E_{cfs} , defined as the energy difference between maxima of the highest and lowest $4f \rightarrow 5d$ bands in the excitation spectra [14, 15]. The magnitude of centroid shift E_c depends mainly on the covalency of the Ce^{3+} -ligand bond and the polarizability of the ligands coordinating Ce^{3+} . The crystal field splitting is defined by the size and shape of the coordination polyhedron around Ce^{3+} [14, 15]. In Table 1, the luminescence characteristics of Ce_I ions in $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ are compared with those of Ce^{3+} ones in $\text{Ca}_2\text{B}_5\text{O}_9\text{Cl}$ [11] and CaBPO_5 [12]. It is seen that the total crystal field splitting E_{cfs} for the Ce_I centers in $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ is relatively low. The observed value of E_c ($\sim 9800 \text{ cm}^{-1}$) for these centers corresponds also to the typical val-

ues for alkaline earth and rare earth phosphates ($8000\text{--}10000 \text{ cm}^{-1}$) and is essentially lower than those for oxides [14, 15]. This implies the high ionicity degree of the metal-ligand bond for this Ce^{3+} -position. When comparing the Stokes shift (δ) of the Ce^{3+} emission in $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ with those for the calcium compounds, it is found that it is quite large. It is well known that when Ce^{3+} ion is incorporated in a lattice in a larger cationic site, the relaxation in the excited state is larger and therefore the Stokes shift is larger.

As mentioned above, Ce^{3+} can substitute for Ca^{2+} in $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ in Ca(I) position with symmetry C_3 or in Ca(II) position with C_S symmetry. Taking into account that the average metal-ligand distance (R) for the Ca(I) position ($R = 2.56 \text{ \AA}$) is essentially larger than that for the Ca(II) position ($R = 2.44 \text{ \AA}$), one can conclude that the dominant center (Ce_I) with emission maxima at 335 and 362 nm consists of a Ce^{3+} ion in the large Ca(I) position. In this case, the charge compensation for Ce^{3+} ions is provided by calcium vacancies, and in samples with relatively high concentrations of Ce^{3+} , a single calcium vacancy will compensate one Ce^{3+} ion distantly and one Ce^{3+} locally. The excitation band at 313 nm can be expected to be due to associates of a calcium vacancy with a Ce^{3+} ion on the Ca(I) position.

The other type of Ce^{3+} centers (Ce_{II}) can be attributed to a Ce^{3+} ion on the Ca(II) position. The charge compensation of Ce^{3+} ions occupying the Ca(II) positions is provided by substitution of OH^- ions by O^{2-} . This mechanism implies the formation of $(\text{Ce}_{\text{Ca}}\text{O}_{\text{OH}})^x$ associates. This can be responsible for the lower-energy position of the Ce_{II} emission band (395 nm) as compared to the Ce_I emission band due to a larger crystal field splitting of the $\text{Ce}^{3+} 5d$ configuration and to strengthening of the covalent bond between Ce^{3+} and its environment.

From the results presented here, it can be concluded that in $\text{Ca}_{10(1-x)}\text{Ce}_{10x}(\text{PO}_4)_6(\text{OH})_2$ solid solutions ($x \leq 0.005$) prepared in a re-

Table 1. Comparison of the luminescence properties of Ce^{3+} ions in calcium compounds.

| Compound | Excitation maxima, nm | E_{cfs} , cm^{-1} | E_c , cm^{-1} | δ , cm^{-1} |
|--|-------------------------|------------------------------|--------------------------|-----------------------------|
| $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ | 202, 221, 249, 265, 291 | 15050 | 9830 | 4200 |
| CaBPO_5 | 194, 210, 238, 258, 286 | 16600 | 8240 | 3520 |
| $\text{Ca}_2\text{B}_5\text{O}_9\text{Cl}$ | 200, 215, 237, 289, 314 | 18150 | 10190 | 1800 |

ducing atmosphere, Ce_1 is the only Ce^{3+} -related center present in significant amounts. In other words, Ce^{3+} ions in calcium hydroxyapatite tend to occupy preferably the Ca(I) sites. Our results and conclusions are consistent with the data presented in literature for natural apatites [16]. The intense UV emission band at about 360 nm in time-resolved luminescence spectra of blue and green apatites has been attributed to Ce^{3+} ions in the Ca(I) site.

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Розподілення та люмінесцентні властивості іонів Ce^{3+} у гідроксіапатиті кальцію

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Вивчено люмінесцентні властивості іонів Ce^{3+} у гідроксіапатиті кальцію $Ca_{10}(PO_4)_6(OH)_2$ при збудженні в області 3,5–15 еВ. Встановлено, що у $Ca_{10}(PO_4)_6(OH)_2$, одержаному у відновлювальному середовищі, іони Ce^{3+} виявляють тенденцію займати високосиметричні Ca(I)-позиції. Визначено енергії всіх компонентів 5d-конфігурації іонів Ce^{3+} у позиціях Ca(I). У спектрі збудження люмінесценції іонів Ce^{3+} , крім 4f→5d смуг, також спостерігається смуга з максимумом 7,7 еВ, що обумовлена власним поглинанням гідроксіапатиту кальцію. Обговорюється вплив структурних особливостей $Ca_{10}(PO_4)_6(OH)_2$ на люмінесцентні властивості іонів Ce^{3+} .