

Luminescence Spectroscopy of Ca-apatites under VUV Excitation

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Apatites found in nature represent the class of materials with very wide functionality. Chemical formula of any apatite can be written generally as $M_4^I M_6^{II} (TO_4)_6 X_2$, where M denotes metal ions (e.g. alkali earth or rare earth) occupying two non-equivalent positions (I and II) in crystal lattice, TO_4 refers to oxyanions with tetrahedron structure (e.g. PO_4 , SiO_4 , GeO_4 , VO_4 , etc) and X anions (OH , F , O , Cl). Consequently, chemical composition of apatites is highly variable, which opens extraordinary possibilities for the synthesis of novel functional materials. Apatites have hexagonal crystal structure [1] where tetrahedrons (TO_4) and metals (M) form positively charged framework with open channels along the hexagonal axis. Electroneutrality of crystal structure is provided by anions (X), which have relatively high mobility in these channels. The latter one makes apatites family analogous to nanoporous compound of $12CaO \cdot 7Al_2O_3$, investigated by us earlier [2], where charge compensating negative species (e.g. O^{2-} situated in pores) possess similar properties. Both compounds are also similar in another aspect because there are multiple sites available for anions and cations (e.g. 4 sites for O and 2 sites for Ca ions in HAP, respectively) in the host lattice. Pure hydroxyapatite (HAP) $Ca_{10}(PO_4)_6(OH)_2$ and its fluorine-substituted modification (FAP; $X=F$) are obviously the most well-known apatites, being the main inorganic constituent of all mammalian bones and teeth, which generates strong interest to use this material in all kind of applications requiring biocompatibility. Fluorinated apatites have attracted much attention due to higher chemical and thermal stability (very useful e.g. in dental applications). Despite of very high potential for various applications (e.g. apatites are effective host lattices for light emitting and laser materials), some basic optical properties of these apatites remain still to be investigated. To the best of our knowledge, even energy gap width of HAP is not reliably determined yet. The main obstacle is the absence of high-purity single crystals for optical studies of HAP. Trace elements and defects present in such complicated host can mask fundamental optical properties. One of a few estimations of HAP band-gap (>6 eV) based on studies of diffuse reflectance was reported recently [3].

In this work we applied luminescence spectroscopy methods to study electronic properties of HAP and FAP including determination of the band-gap energy by photostimulated luminescence (PSL) method described in [4]. Measurements were performed at the SUPERLUMI station of HASYLAB at DESY (Hamburg, Germany) and using the FINEST branch-line of I3 at the MAX-III storage ring (Lund, Sweden). Samples of HAP were prepared using commercial powder (Sigma-Aldrich, 99.999% grade), which was pressed (12 t/cm²) into pellets ($\varnothing 7$ mm, ≈ 1 mm thickness) and treated in ambient atmosphere at 1100 °C for 2 h resulting in dense ceramics. Some of the pellets were treated in oxygen atmosphere (denoted as HAPox). The FAP ceramics were synthesized using solid state reaction of β -tricalciumphosphate ($Ca_3(PO_4)_2$) and CaF_2 at 1300 °C for 5 h in Ar. Micro-Raman studies performed showed that both HAP and FAP samples showed identical vibrational spectra with ones reported in [1], confirming the phase purity of studied samples prepared by us.

Emission and photoluminescence excitation spectra of HAP, HAPox and FAP together with afterglow creation spectrum were measured at 10 K (see Figure 1). The intrinsic emissions of these compounds are located in UV, being due to radiative decay of Frenkel excitons localized on the PO_4 oxyanions. The well-pronounced excitation bands at 7.2 eV and 7.5 eV in HAPox and FAP, respectively were interpreted as transitions within PO_4 oxyanion complexes in agreement with earlier studies (e.g. see [5] and references therein). Theoretical study [6] showed also that the density of PO_4 states is responsible for lowest energy transitions in HAP. The valence band of HAP is formed of P(2p,3p,3d) and O(2s,2p) states and transitions to the Ca 3d states near conduction band bottom can determine energy gap width. Excitation onsets of photoluminescence and afterglow spectra enabled us to determine tentatively the band-gap energy for pure HAP as $E_g \approx 7.7$ eV, which is in good correspondence with the energy gap value 8 eV of the β - $Ca_3(PO_4)_2$ [7]. Comparison of excitation spectra allows to allocate the energy gap of FAP at least 0.5 eV higher than that of HAP, whereas the DFT calculations predict difference of 0.9 eV [6]. Since F^- ion is

smaller than OH⁻ group, the transition from HAP to FAP causes contraction in the *a*-axes dimensions [1] and, consequently, considerable changes of the electronic structure (including the increase of value of energy gap) manifest themselves in intrinsic emission and its excitation spectra.

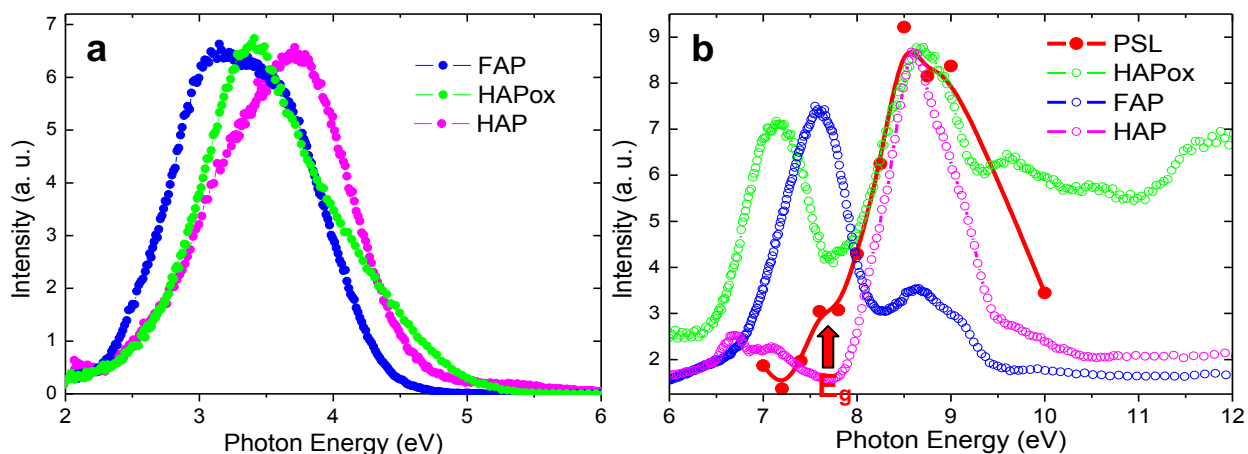


Figure 1: a – normalised emission spectra of HAP, HAPox and FAP at 10 K under excitation by $E_{exc} > E_g$ photons; b – excitation spectra (for 3.8 eV band of HAP – magenta circles, for 3.4 eV band of HAPox – green circles and for 3.0 eV band of FAP – blue circles) and afterglow creation spectrum of HAP at 10 K. Spectra have different intensity scales for better qualitative visualization of results.

The introduction of O⁻ ions as anions by thermochemical processing of HAP in oxygen atmosphere causes significant changes in the spectra of HAPox. Under excitation above E_g its emission spectrum has a maximum at 3.4 eV, whereas the maxima FAP and HAP emission lie at lower (3.2 eV) and higher energies (3.8 eV), respectively. Even more notable changes are visible in the low energy part of excitation spectra of HAPox and HAP. The excitation onset is at 6.4 eV for both materials. In comparison with a dominating feature at 8.6 eV the first weak band covering range of 6.4-7.6 eV has a doublet structure in HAP being much less pronounced than that in HAPox. The band structure calculations [6] have shown that near the top of valence band hydroxyl group causes appearance of additional states, which are due to the O⁻ ion of OH⁻ group. Even though there are no theoretical data on the apatite compound, where O⁻ acts as an anion, one can assume by analogy that a contribution of such states can be even stronger. Thus it is in agreement with the experimental data on HAPox, where the intensity of first excitation band at 7.15 eV is about 80 % of the major one at 8.6 eV. Also the role of oxygen states is rather significant on formation of Frenkel type self-trapped excitons, where its hole component is localized on oxygen ions of PO₄ tetrahedra. Additional contribution of electronic states due to O⁻ ions located in the channel near PO₄ group can facilitate the formation of self-trapped excitons and improve energy transfer through electron-hole processes. In HAPox the intrinsic luminescence (see Fig. 1b) continues to be efficiently excited at higher energies (< 9.2 eV), while in HAP and FAP such energy transfer mechanism is suppressed. We tentatively assign the origin of this process to the increased hole mobility due to channel O⁻ ions.

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References

- [1] M. Wei, J.H. Evans, T. Bostrom, L.Grøndahl, J. Mat. Sci.: Mat. Med. **14** (2003) 311.
- [2] E. Feldbach, V. P. Denks, M. Kirm, K. Kunnus, A. Maaros, Radiat. Meas. **45** (2010) 281.
- [3] M. Tsukada, M. Wakamura, N. Yoshida, T. Watanabe, J. Mol. Catal. A (2010)
doi:10.1016/j.molcata.2011.01.017
- [4] V. Nagirnyi, L. Jönsson, M. Kirm, *et al.*, Radiat. Meas. **38** (2004) 519.
- [5] Q. Zeng, H. Liang, G. Zhang, *et al.*, J. Phys.: Condens. Matter **18** (2006) 9549
- [6] P. Rulis, L. Ouyang, W. Y. Ching, Phys. Rev. B **70** (2004) 155104.
- [7] Ch. Lushchik, T. Savikhina, I. Meriloo and H. Soovik, Trudy Inst. Fiziki AN ESSR **58** (1986) 123.