



INTERNATIONAL CONFERENCE
MEĐUNARODNA KONFERENCIJA

MEETING POINT OF THE SCIENCE AND PRACTICE IN THE FIELDS OF
CORROSION, MATERIALS AND ENVIRONMENTAL PROTECTION

*STECIŠTE NAUKE I PRAKSE U OBLASTIMA KOROZIJE,
ZAŠTITE MATERIJALA I ŽIVOTNE SREDINE*

PROCEEDINGS

KNJIGA RADOVA

Under the auspices of the
MINISTRY OF EDUCATION, SCIENCE AND TECHNOLOGICAL
DEVELOPMENT OF THE REPUBLIC OF SERBIA

Pod pokroviteljstvom
MINISTARSTVO PROSVETE, NAUKE I TEHNOLOŠKOG RAZVOJA
REPUBLIKE SRBIJE

September 13-16, 2021 : : Tara Mountain, Serbia

CIP - Katalogizacija u publikaciji
Narodna biblioteka Srbije, Beograd

620.193/.197(082)(0.034.2)

621.793/.795(082)(0.034.2)

667.6(082)(0.034.2)

502/504(082)(0.034.2)

66.017/.018(082)(0.034.2)

INTERNATIONAL Conference YUCORR (22 ; 2021 ; Tara)

Meeting point of the science and practice in the fields of corrosion, materials and environmental protection [Elektronski izvor] : proceedings = Stecište nauke i prakse u oblastima korozije, zaštite materijala i životne sredine : knjiga radova / XXII YuCorr International Conference = XXI YuCorr [Jugoslovenska korozija] Međunarodna konferencija, September 13-16, 2021, Tara Mountain, Serbia = [organized by] Serbian Society of Corrosion and Materials Protection ... [et al.] ; [organizatori Udruženje inženjera Srbije za koroziju i zaštitu materijala ... [et al.] ; [editors, urednici Miomir Pavlović, Miroslav Pavlović, Marijana Pantović Pavlović]. - Beograd : Serbian Society of Corrosion and Materials Protection UISKOSAM : Udruženje inženjera Srbije za koroziju i zaštitu materijala UISKOSAM, 2021 (Beograd : Serbian Society of Corrosion and Materials Protection UISKOSAM : Udruženje inženjera Srbije za koroziju i zaštitu materijala UISKOSAM). - 1 elektronski optički disk (CD-ROM) ; 12 cm

Sistemska zahteva: Nisu navedeni. - Nasl. sa naslovne strane dokumenta. - Tekst na engl. i srp. jeziku.

- Tiraž 200. - Bibliografija uz većinu radova. - Abstracts.

ISBN 978-86-82343-28-8

a) Премази, антикорозиони -- Зборници б) Превлаке, антикорозионе -- Зборници в)

Антикорозиона заштита -- Зборници г) Животна средина -- Заштита -- Зборници д) Наука о материјалима -- Зборници

COBISS.SR-ID 48091145

XXII YUCORR – International Conference | Međunarodna konferencija

PUBLISHED AND CD BURNED BY | IZDAVAČ I NAREZIVANJE CD

SERBIAN SOCIETY OF CORROSION AND MATERIALS PROTECTION (UISKOSAM)

UDRUŽENJE INŽENJERA SRBIJE ZA KORZIJU I ZAŠTITU MATERIJALA (UISKOSAM),

Kneza Miloša 7a/II, 11000 Beograd, Srbija, tel/fax: +381 11 3230 028, office@sitzam.org.rs; www.sitzam.org.rs

FOR PUBLISHER | ZA IZDAVAČA Prof. dr MIOMIR PAVLOVIĆ, predsednik UISKOSAM

SCIENTIFIC COMMITTEE | NAUČNI ODBOR: Prof. dr M. G. Pavlović, Serbia – President

Prof. dr Đ. Vaštag, Serbia; Dr M. M. Pavlović, Serbia; Prof. dr D. Vuksanović, Montenegro;

Prof. dr D. Čamovska, North Macedonia; Prof. dr M. Antonijević, Serbia; Prof. dr S. Stopić, Germany;

Prof. dr R. Zejnilović, Montenegro; Prof. dr L. Vrsalović, Croatia; Dr N. Nikolić, Serbia;

Dr I. Krastev, Bulgaria; Prof. dr B. Grgur, Serbia; Prof. dr M. Gvozdrenović, Serbia;

Prof. dr S. Hadži Jordanov, North Macedonia; Prof. dr R. Fuchs Godec, Slovenia;

Prof. dr J. Stevanović, Serbia; Dr V. Panić, Serbia; Dr M. Mihailović, Serbia;

Prof. dr V. Marić, Bosnia and Herzegovina; Prof. dr J. Jovičević, Serbia; Prof. dr D. Jevtić, Serbia;

Dr F. Kokalj, Slovenia; Prof. dr A. Kowal, Poland; Prof. dr Prof. dr M. Gligorić, Bosnia and Herzegovina;

Prof. dr M. Tomić, Bosnia and Herzegovina; Prof. Dr B. Arsenović, Bosnia and Herzegovina

ORGANIZING COMMITTEE | ORGANIZACIONI ODBOR: Dr Miroslav Pavlović – president

Dr Nebojša Nikolić – vice president; Dr Marija Mihailović – vice president

Prof. dr Miomir Pavlović; Aleksandar Putnik B.Sc.; Dr Vladimir Panić; Jelena Slepčević, B.Sc.;

Dr Vesna Cvetković; Prof. dr Milica Gvozdrenović; Zagorka Bešić, B.Sc.; Gordana Miljević, B.Sc.;

Miomirka Anđić, B.Sc.; Dr Marija Matić; Marijana Pantović Pavlović, M.Sc.; Dr Dragana Pavlović;

Dr Sanja Stevanović; Lela Mladenović – secretary

EDITORS | UREDNICI: Prof. dr Miomir Pavlović, Dr Miroslav Pavlović, Marijana Pantović Pavlović, M.Sc.

SCIENTIFIC AREA | OBLAST: CORROSION AND MATERIALS PROTECTION | KOROZIJA I ZAŠTITA MATERIJALA

PAGE LAYOUT | KOMPJUTERSKA OBRADA I SLOG: Dr Miroslav Pavlović

CIRCULATION | TIRAŽ: 200 copies | primeraka

PUBLICATION YEAR | GODINA IZDANJA: 2021

ISBN 978-86-82343-28-8



Ovaj PDF fajl sadrži elektronsku Knjigu radova prezentovanih u okviru Međunarodne konferencije **XXII YuCorr**. U knjizi su **plavom bojom** obeleženi aktivni linkovi ka pojedinim njenim delovima, iz Sadržaja do naznačenih stranica.

This PDF file contains Proceedings presented on the **XXII YuCorr** International Conference. It can be easily navigated through the book contents by a single click on the appropriate links in Contents (**showed in blue**).

Autori snose punu odgovornost za sadržaj, originalnost, jezik i gramatičku korektnost sopstvenih radova.

Authors bear full responsibility for the content, originality, language and grammatical correctness of their own works.

**XXII YUCORR IS ORGANIZED BY
ORGANIZATORI XXII YUCORR-a**



SERBIAN SOCIETY OF CORROSION AND MATERIALS PROTECTION

Udruženje Inženjera Srbije za Koroziju i Zaštitu Materijala



**INSTITUTE OF CHEMISTRY, TECHNOLOGY AND METALLURGY,
UNIVERSITY OF BELGRADE**

*Institut za Hemiju, Tehnologiju i Metalurgiju,
Univerzitet u Beogradu*



UNION OF ENGINEERS AND TECHNICIANS OF SERBIA, BELGRADE

Savez Inženjera i Tehničara Srbije



ENGINEERING ACADEMY OF SERBIA

Inženjerska Akademija Srbije

**XXII YUCORR IS ORGANIZED UNDER THE AUSPICES OF THE
MINISTRY OF EDUCATION, SCIENCE AND TECHNOLOGICAL
DEVELOPMENT OF THE REPUBLIC OF SERBIA**



***XXII YUCORR JE FINANSIJSKI POMOGLO
MINISTARSTVO PROSVETE, NAUKE I TEHNOLOŠKOG RAZVOJA
REPUBLIKE SRBIJE***

SPONSORS | SPONZORI

INTERNATIONAL SOCIETY OF ELECTROCHEMISTRY, Switzerland

SAVEZ INŽENJERA I TEHNIČARA SRBIJE, Beograd

HELIOS SRBIJA a.d., Gornji Milanovac

METAL CINKARA d.o.o., Inđija

SURTEC ČAČAK d.o.o., Čačak

ALFATERM d.o.o., Čačak

INSTITUT ZA PREVENTIVU d.o.o., Novi Sad

EKP ELKER a.d., Prijedor, Republika Srpska, B&H

EKO ZAŠTITA d.o.o., Bijeljina, Republika Srpska, B&H

IPIN d.o.o., Bijeljina Republika Srpska, B&H

HEMIPRODUKT d.o.o., Novi Sad

INSTITUT ZA OPŠTU I FIZIČKU HEMIJU, Beograd

SZR "GALVA", Kragujevac

NOVOHEM d.o.o., Šabac

Table of Contents

PLENARY LECTURES PLENARNA PREDAVANJA	1
Environmental protection with natural zeolite – a circular economy approach Nediljka Vukojević Medvidović	2
Where is biodiesel technology going – a critical view on raw materials, catalysts and processes Vlada Veljković	3
Raw Materials Supply in Future - A Duck Soup Issue??? Svetomir Hadži Jordanov	5
Optimization of preventive activities and maintenance of water wells exposed to corrosion and encrustation processes Vaso Novaković, Nikola Nikolić	6
INVITED LECTURES PREDAVANJA PO POZIVU	7
New Porous Coordination Polymers Based on 3d Metal Ions Traian-Dinu Pasatoiu, Radu Cristian Dascalu, Catalin Maxim, Marius Andruh	8
Photosynthetic efficiency and morphological damage symptoms of <i>Juglans regia</i> L. leaves in urban environment Dragana Pavlović, Marija Matić, Veljko Perović, Zorana Mataruga, Milica Marković, Miroslava Mitrović, Pavle Pavlović	9
Comparison of bioactivity, cytotoxicity, antimicrobial and corrosive behavior of ceramic coatings with and without polymer on titanium Marijana R. Pantović Pavlović, Miroslav M. Pavlović, Jasmina S. Stevanović, Vladimir V. Panić, Nenad L. Ignjatović	19
ORAL PRESENTATIONS USMENA SAOPŠTENJA	31
Electrochemical properties of pigment extracts from dark red corn grains Maja Stevanović, Jelena Lović, Sanja Stevanović, Marija Mihailović	32
Electrochemical quantitative determination of sertraline in pharmaceutical formulation using a gold electrode in bicarbonate solution Jelena Lović, Dušan Mijin, Milka Avramov Ivić	37
Ecophysiological response of <i>Tilia sp</i> and <i>Pinus nigra</i> to Pb in urban environment Marija Matić, Dragana Pavlović, Veljko Perović, Dragan Čakmak, Miroslava Mitrović, Pavle Pavlović	42
Bacterial nanocellulose as green support for platinum catalysts in methanol electrooxidation reaction Sanja Stevanović, Marijana Ponjavić, Jasmina Nikodinović Runić, Vesna Maksimović, Vladan Ćosović	49
Application of Collaborative Robots in the Fourth Industrial Revolution - Industry 4.0 Isak Karabegović, Edina Karabegović, Ermin Husak, Mehmed Mahmić	51
Protection against electrochemical corrosion of steel tank floors by installing a cathodic protection system Željko Krivačević, Dejan Grgić, Saša Stojanović, Aleksandar Pešić	60

Research on The Application of Mobile Robots for Disinfection of Contaminated Space With Virus "Covid-19"	
Isak Karabegović, Ermin Husak, Lejla Mehmedović Banjanović, Safet Isić	66
Aqueous electrolyte polypyrrole zinc cell with supercapattery performance	
Marija Janačković, Milica Gvozdenović, Branimir Jugović, Branimir Grgur	75
Testing the effectiveness of raspberry flower extract as an inhibitor of copper's corrosion in 3%NaCl	
Dejana Kasapović, Fehim Korać, Farzet Bikić	76
Fabrication and characterization of manganese ferrite/expanded vermiculite as a magnetic adsorbent of nickel ions	
Mladen Bugarčić, Miroslav Sokić, Branislav Marković, Milan Milivojević, Aleksandar Marinković, Jovana Perendija, Zorica Lopičić	84
POSTER PRESENTATIONS I POSTERSKA SAOPŠTENJA	95
Impact of Noise During the Reconstruction of The Section of the Tivat-Jaz Main Road and During Traffic on the Local Population	
Darko Vuksanović, Dragan Radonjić, Jelena Šćepanović	96
Level of Environmental Quality Improvement by Disposal of Municipal Waste in Sanitary Cell	
Jelena Šćepanović, Darko Vuksanović, Dragan Radonjić	103
Analysis of the Possibility of Collection, Transport, Storage and Processing of Waste Tires in Order to Improve the Quality of the Environment	
Dragan Radonjić, Darko Vuksanović, Jelena Šćepanović	114
Commercial food supplements of 'bee products' as inhibitors of corrosion processes	
Regina Fuchs–Godec, Marija Riđošić, Milorad. V. Tomić, Miomir G. Pavlović	126
Thin TiO ₂ -based coatings for the purpose of corrosion protection	
Regina Fuchs–Godec	131
Influence of recasting on the structure and properties of Ni-Cr dental alloy	
Vesna M. Maksimović, Aleksandra D. Čairović, Ivana Lj. Cvijović-Alagić	136
Synthesis and characterization of silver-doped ceria nanopowders	
Branko Matović	137
Microstructural refinement influence on the Ti-45Nb alloy properties in physiological conditions	
Ivana Cvijović-Alagić, Slađana Laketić, Dejan Zagorac, Jelena Bajat, Đorđe Veljović, Vesna Kojić, Marko Rakin	138
The influence of self-doping on electrochemical synthesis and behaviour of polyaniline	
Milica Gvozdenović, Branimir Jugović, Bojan Jokić, Enis Džunuzović, Branimir Grgur	139
Electrodeposition of Nd and Pr onto W from fluoride based melts	
Vesna S. Cvetković, Dominic Feldhaus, Nataša M. Vukićević, Nebojša D. Nikolić, Bernd Friedrich, Jovan N. Jovićević	140
Influence of regime of electrolysis on morphology and structure of copper dendrites	
Nebojša D. Nikolić, Vesna M. Maksimović, Zvezdana Baščarević, Predrag M. Živković, Miomir G. Pavlović	145
Low cost hydrothermal synthesis of shining carbon quantum dots	
Biljana Babić, Ana Kalijadis, Marko Nikolić, Martina Gilić, Branislav Jelenković, Bojan Jokić	146

Chemometric approach in the monitoring of the TiNi alloy corrosion behaviour under different coastal conditions Đendi Vaštag, Špiro Ivošević _____	147
The influence of electrolyte temperature on corrosion of CuAlMnZn alloy in Na ₂ SO ₄ solution Ladislav Vrsalović, Senka Gudić, Ines Garvanović, Dražan Jozić, Ivana Ivanić, Mirko Gojić, Stjepan Kožuh _____	148
New biomedical materials based on metal-doped fluorapatite Dusan Milojkov, Vaso Manojlovic, Miroslav Sokic _____	159
Influence of Current Density and Ultrasound on the Morphology and Roughness of Zn-Mn-CeO ₂ Nanocomposite Coatings Marija Riđošić, Mihael Bučko, Regina Fuchs Godec, Milorad Tomić, Jelena Bajat, Miomir Pavlović _____	166
Solvent Extraction of Copper From Oxide Ore By Organic Extragens Branko Bojić, Ljubica Vasiljević, Danijela Rajić _____	167
Corrosion protection of ship structures Srđan Bulatović, Vujadin Aleksić, Bojana Zečević _____	177
Oil Recovery from Roadside Pennycress (Thlaspi Alliaceum L.) Seeds and its Application for Biodiesel Production Milan Kostić, Olivera Stamenković, Vlada Veljkovi¹ _____	183
Precipitation behaviour in pH adjusted lateritic ore solution Jonas Mitterecker, Marija Mihailović, Milica Košević, Jasmina Stevanović, Srečko Stopić, Vladimir Panić, Bernd Friedrich _____	190
Electrochemical investigation of lateritic ore leachates for metal ions extraction Jonas Mitterecker, Milica Košević, Marija Mihailović, Jasmina Stevanović, Srečko Stopić, Bernd Friedrich, Vladimir Panić _____	195
Synthesis and Characterization of New Coordination Polymers Obtained Using 3d and 3d-4f Nodes Traian-Dinu Pasatoiu, Catalin Maxim, Augustin Madalan, Marius Andruh _____	199
Method development and removal study of amoxicillin by RP-HPLC Maria Uzelac, Katarina Modić, Nemanja Banić _____	199
Removal of methyl orange using combined ZnO/Fe ₂ O ₃ /ZnO-Zn composite coated to the aluminium foil in the presence of simulated solar radiation Nemanja Banić, Jugoslav Krstić, Maria Uzelac _____	211
Overview of Fuel A-1 and Lubricants for Mlas Motors Božidarka Arsenović, Darinka Jevtić, Zorica Ristić _____	223
Damage and Defects in Welded Joints Emina Dzindo, Rodoljub Milicevic _____	234
Mechanisms and morphologies of cavitation damage of NN 70 steel Vujadin Aleksić, Marina Dojčinović, Ljubica Milović, Bojana Aleksić, Ana Prodanović _____	237
Electrochemical examination of the pyrocatechol influence on the Bray-Liebafsky reaction after the oscillatory period Jelena P. Maksimović, Maja C. Pagnacco _____	249
SPONSORS SPONZORI _____	255

New biomedical materials based on metal-doped fluorapatite ***Novi biomedicinski materijali na bazi metal dopiranih fluorapatita***

Dusan Milojkov^{1,*}, Vaso Manojlovic², Miroslav Sokic¹

¹ *Institute for Technology of Nuclear and Other Mineral Raw Materials, Belgrade, Serbia*

² *Faculty of Technology and Metallurgy, University of Belgrade, Serbia*

* *d.milojkov@itnms.ac.rs*

Abstract

In this paper, metal substitutions in the fluorapatite crystal matrix will be presented in order to obtain a new type of biomedical material. Fluorapatite has been intensively tested in recent decades as a building material for luminescent materials for many applications, from fluorescent lamps, through LEDs, to nanomaterials for high-tech biomedical applications. Fluorapatite has been shown to be non-toxic, extremely chemically stable and corrosion-resistant, as well as biocompatible, bioactive and osteoconductive. Also, fluorapatite proved to be a great host material for doping luminescent centers in the form of trivalent ions of rare earth and transition metals. Thanks to the position of the fluorine atom in the structure of the crystal lattice of fluorapatite, in the center of the Ca₂ triangle (6h position) in the mirror planes at $z = 1/4$ and $z = 3/4$, this structure is extremely stable and stable. Also, the fluorine atom is responsible for the fact that fluorapatite, unlike hydroxyapatite, shows antibacterial properties. By touching different metals into this low phonon energy matrix, luminescent materials can be constructed that will emit light in the ultraviolet, visible or infrared region of the electromagnetic spectrum. If all these properties of fluorapatite are taken into account, their combination can lead to new materials for a wide range of biomedical applications.

Keywords: *fluorapatite; metals; luminescence; biomedical nanomaterials.*

Izvod

U ovom radu biće prikazane supstitucije metala u kristalnom matriksu fluorapatita s ciljem dobijanja nove vrste biomedicinskih materijala. Fluorapatit se poslednjih decenija intenzivno ispituje kao materijal za izgradnju luminiscentnih materijala za široki spektar primena, od fluorescentnih lampi, preko LED dioda, do nanomaterijala za biomedicinske aplikacije visoke tehnologije. Fluorapatit se pokazao kao netoksičan, izuzetno hemijski stabilan i otporan na koroziju, a uz to i biokompatibilan, bioaktivan i osteokonduktivan. Takođe, fluorapatit se pokazao i kao sjajan materijal domaćin za dopiranje luminiscentnih centara u vidu trovalentnih jona retkih zemalja i prelaznih metala. Zahvaljujući položaju atoma fluora u strukturi kristalne rešetke fluorapatita, u centru Ca₂ trougla (6h položaj) u ogledalskim ravnima na $z = 1/4$ i $z = 3/4$, ovakva struktura je izuzetno stabilna i postojana. Takođe, atom fluora je odgovoran što fluorapatit, za razliku od hidroksiapatita, pokazuje i antibakterijska svojstva. Dopiranjem različitih metala u ovu matricu niske fononske energije, mogu se konstruisati luminiscentni materijali koji će emitovati svetlost u ultravioletnoj, vidljivoj ili infracrvenoj oblasti elektromagnetnog spektra. Ako se uzmu u obzir sve ove osobine fluorapatita, njihovom kombinacijom mogu se dobiti novi materijali za široki spektar biomedicinskih primena.

Ključne reči: *fluorapatit; metali; luminescencija; biomedicinski nanomaterijali.*

Introduction

In recent years, various nanomaterials based on metal-doped apatites have been synthesized and tested for many biomedical applications [1-4]. Apatites have the general formula of unit cell

$\text{Ca}_{10}(\text{PO}_4)_6\text{X}_2$, where component X is represented by anions of fluorine (F^-), chlorine (Cl^-) and hydroxyl groups (OH^-), so that fluorapatite [$\text{Ca}_5(\text{PO}_4)_3\text{F}$], chlorapatite [$\text{Ca}_5(\text{PO}_4)_3\text{Cl}$] and hydroxyapatite [$\text{Ca}_5(\text{PO}_4)_3\text{OH}$] (each with $z=2$ (two molecular formulas)) are three phases of these naturally occurring minerals [1]. The most common phase in nature is fluorapatite and makes up about 95% of apatite rocks [2]. Apatites are subject to various isomorphous substitutions, so the composition of apatite in nature differs from these ideal compositions.

Fluorapatite, together with hydroxyapatite, is used as a biomaterial for bone repair because it has a similar structure as the inorganic component of bones and teeth in living organisms [3, 4]. In addition to that suitable structural fluorapatite, it also shows biocompatible, bioactive and antibacterial properties [4]. Compared to hydroxyapatite, it has better physicochemical properties, such as high melting temperature, poor solubility in acids, corrosion resistance [3]. Fluorapatite doped with rare earth and metal ions has therefore been tested in recent years as a material for use in biomedicine for bone tissue engineering, biomarking and bioimaging [5, 6, 7, 8]. As fluorapatite is similar to bone tissue, the interaction of fluorapatite with radioactive radiation for use as a dosimeter in medicine and environmental protection has also been conducted in recent years [9].

Due to the possibility of a wide range of applications, fluorescent materials based on fluorapatite have attracted a lot of attention from researchers in recent decades. One of the main characteristics of apatite crystals is the capacity of the structure to withstand many ionic substitutions. The crystal structure of fluorapatite is a potentially significant matrix for optically active trivalent ions of rare earth, due to the highly pronounced crystal field that allows luminescent transitions of electrons from the orbital [10]. Due to all these properties, fluorapatite doped with rare earth ions has found application in UV lamps, LEDs for display and plasma TVs and lasers [10, 11, 12, 13].

Crystal structure of fluorapatite and luminescence

Fluorapatite (FAP), $\text{Ca}_5(\text{PO}_4)_3\text{F}$, is the most stable apatite phase, the least soluble, and the hardest of all apatite structures. On the Moss scale, the hardness is 5. FAP crystallizes hexagonal in the spatial group P63/m (number 176) with the parameters of the unit cell $a = 9,367 (1) \text{ \AA}$, $c = 6,884 (1) \text{ \AA}$, $z = 2$ (Figure 1) [14 -16]. These unit cell parameters largely depend on the synthesis process.

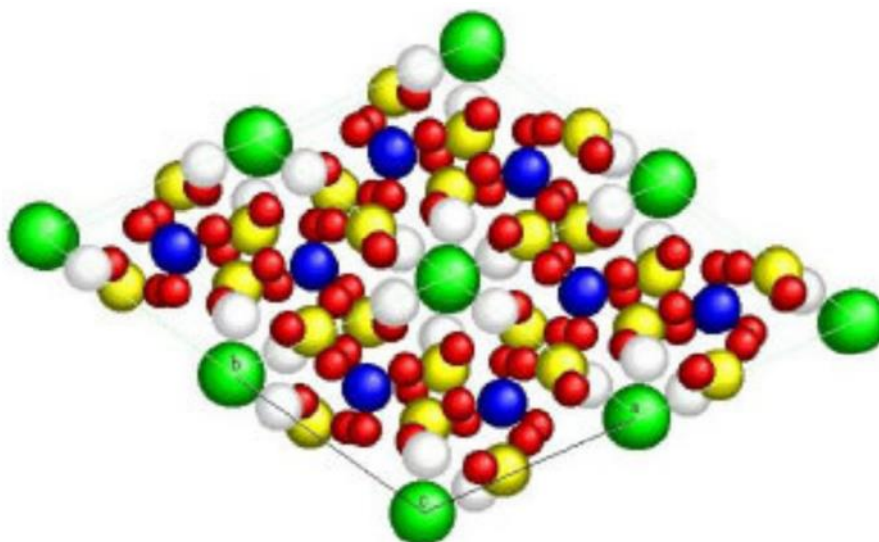


Figure 1. Arrangement of atoms in the fluorapatite crystal (projection on (001)). The P atom is colored yellow, the O atoms are red, the Ca1 is blue, the Ca2 is white, and the F atom is green [17].

As many authors have shown, concluding with Hughes et al., The structure of fluorapatite can be described as a hexagonal network composed of PO_4 tetrahedra with calcium (Ca) in interstitial positions and fluoride (F^-) anion columns oriented along with the crystallographic axis c (Figure 1.) [14-16].

The structure of FAP is constructed by ten calcium atoms arranged in two symmetrically different crystallographic positions Ca1 (4f) and Ca2 (6h) [16]. In the Ca1 (4f) position, each calcium atom is surrounded by nine oxygen atoms originating from the PO_4 groups, with the Ca ions themselves bonding to each other in columns parallel to the crystallographic c -axis (Figure 2). The remaining six calcium atoms are in the Ca2 position (6h) and form equilateral triangles around the axis at $z=1/4$ and $z=3/4$ within the mirror planes. Unlike the Ca1 position, the calcium atoms in the Ca2 position are surrounded by six oxygen atoms originating from the surrounding PO_4 groups and with one F atom located in the channel. These F^- ions are located in the center of the Ca2 triangle (6h position) in the mirror planes at $z = 1/4$ and $z = 3/4$ (Figure 2).

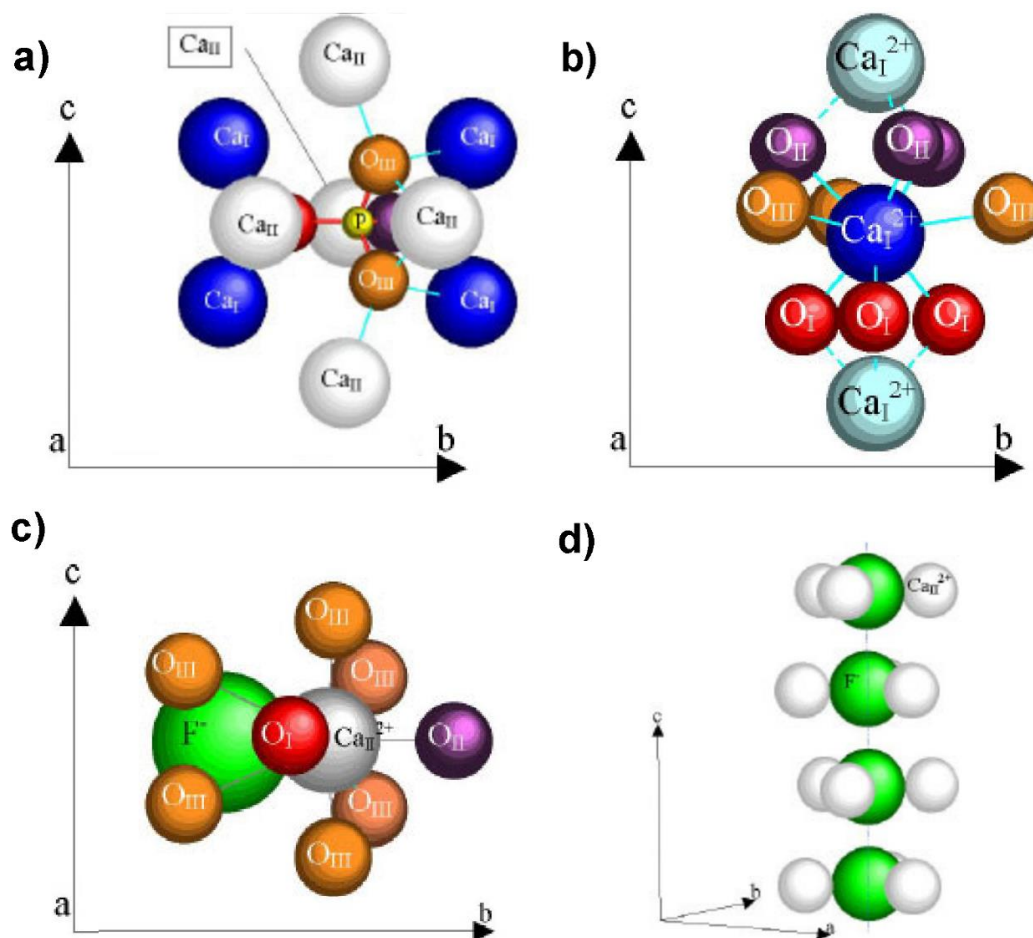


Figure 2. (a) Tetrahedron PO_4 with the environment in FAP crystal lattice. (b, c) Ca_1O_9 and Ca_2O_6F polyhedra for FAP structure. (d) Bonding F atoms in a column surrounded by Ca2 atoms [17].

The apatite crystal lattice is formed of three types of polyhedra, in which changes occur when the anionic members in the columns change. These three polyhedra are shown in Figure 2. a, b, c. Phosphorus occurs in apatite in tetrahedral coordination with the central P atom in the 6h special position (Figure 2.a) [15]. The phosphorus atom (charge: +5) as a central atom is connected to 4 oxygen atoms (charge: -2). The various anions that can be in the columns have a significant impact

on this rigid polyhedron. This primarily refers to the substitution of F anions with OH^- , Cl^- , CO_3^{2-} anions.

Ten calcium ions appear in a unit cell in the form of two different polyhedra Ca1O_9 and $\text{Ca2O}_6\text{F}$. The Ca1O_9 polyhedron with a central cation in the $4f(1/3, 2/3, z)$ position is coordinated with nine oxygen atoms arranged in a three-pointed trigonal prism [15]. In the $\text{Ca2O}_6\text{X}$ polyhedron, Ca2 in a special position binds six oxygen atoms (O1, O2, and $4 \times \text{O}_3$) and one anion in column X for $6h$ in the $\text{P6}_3/\text{m}$ space group [15].

By combining the three polyhedra, an FAP network is formed (Figure 1) when the Ca1 atoms are previously connected along the c-axis in the column by connecting above and below over three oxygen atoms lying in the mirror planes.

So far, we have obtained fluorapatite nanocrystals synthesized in the laboratory by relatively simple methods of precipitation and neutralization [18, 19]. Nanometer-sized single-phase FAP crystals were obtained. By excitation of the obtained powders with different wavelengths at room temperature, emission occurs in the area of purple-blue light of the visible part of the spectrum (Figure 3).

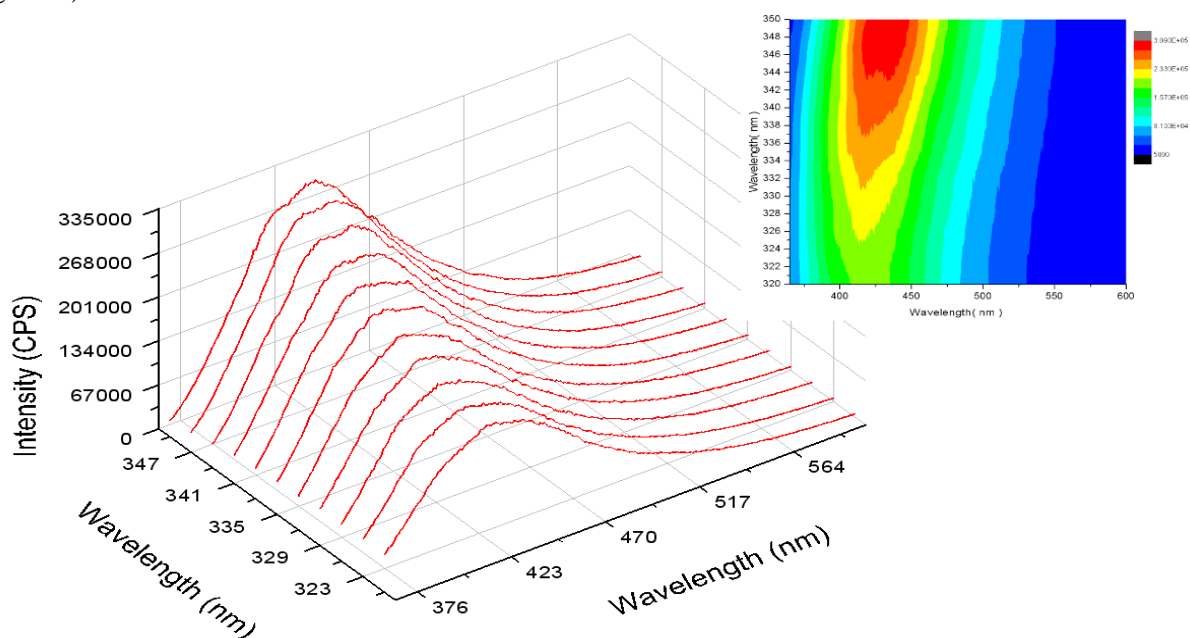


Figure 3. Excitation-emission profile for FAP nano-powder with a separate map [20].

In order to create a model system for quantum chemical calculations that can reproduce the fluorescent spectra of doped fluorapatite, an analysis of crystal structures obtained from the crystal structure database of the American Mineralogist was performed. *Ab initio* calculations of fluorescent spectra were done for three geometries. A model system containing three metal cations, three PO_4^{3-} ions, and an F ion in the center (luminescent center) showed the best agreement with the experimental data [1]. The luminescence of the crystal lattice of FAP originates from the F atom at the $6h$ position at $z = 1/4$ and $3/4$.

Metal substitutions in the crystal matrix of fluorapatite

The crystal lattice of fluorapatite is tolerant to various isomorphous substitutions, so fluorapatite mineral compositions differ in nature from these ideal compositions. The most common form of substitution encountered is called Type-A substitution [17]. This type of substitution refers to substituting the position of the F⁻ anion with other monovalent or divalent anions (type Cl^- , OH^- , CO_3^{2-} ...), but also neutral molecules (H_2O , O_2) [17]. Also, Type-A substitution refers to

substitutions of Ca^{2+} ion position in FAP structure with monovalent, divalent, and trivalent cations (Na^+ , Cu^{2+} , Eu^{3+} ...). The second type of FAP lattice substitution is Type-B substitution and refers to the substitution of the position of the PO_4^{3-} group, most often with CO_3^{2-} groups, but also with complex anions of the MO_4^{3-} type [17]. Finally, some dopants, such as Sb^{3+} and Mn^{2+} , do not substitute the FAP structure in a particular position but occur in special positions that modify the crystal structure. Very often in apatite occurs the so-called. coupled substitution involving the replacement of ions of the same charge (positive or negative) but of a different oxidation state, with electroneutrality being achieved by forming vacancies or replacing ions of the opposite charge [10]. All of these FAP substitutions exist in nature and most of them can be reproduced in laboratory conditions.

Ca^{2+} ion substitutions are most often present in industrial applications when fluorapatite doped with transition metal ions or rare earths are used to manufacture fluorescent lamps. Depending on the position in which the Ca^{2+} substitution was performed, three types of calcium ion substitution were found. Thus Ca^{2+} may be substituted in the Ca1 or Ca2 position, or in both positions. In general, if the substituent does not have a charge equivalent to 2+, there will be a shift to the Ca2 position, which will disturb this position. If the substituent is in the form of M^{2+} , then the substitution depends on the relative size of the substituent and the Ca^{2+} ion. According to Kreidler, the radius of the ion that substitutes for Ca^{2+} ions can be between 0.95 and 1.35 Å [21].

Substitution of Ca^{2+} by monovalent cations (K^+ , Na^+) occurs frequently at the Ca1 position, creating a vacancy at the Fi position sometimes at the Ca1 position. Generally larger cations have a higher affinity for the Ca1 position [22]. In the case of Ag^+ ion substitutions, it is assumed that they change Ca1 positions, with the AB type of CO_3^{2-} substitution due to the charge balance [19].

If the substituent is a divalent cation (e.g. Sr^{2+} , Pb^{2+} , Mg^{2+}), the substitution priority will be the Ca2 position [23]. At the same time, it was noticed that there is no loss of PO_4^{3-} ions, and the degree of change is generally small. In the same way, if both Ca^{2+} (Ca1 and Ca2) positions are substituted with Pb^{2+} or Cd^{2+} , the crystal lattice will not undergo any major structural change [24, 25]. Only an increase in unit cell parameters and M-O distance was observed. On the other hand, the substitution of divalent cations only in the Ca1 position has many consequences per crystal structure. The crystal symmetry will be broken and the spatial group becomes $P63$. Therefore, Mn^{2+} cations are considered to perform FAP lattice substitutions at special positions.

Substitution of Ca^{2+} with trivalent cations (Sb^{3+} , Nd^{3+}) is relatively rare in nature, but this type of substitution is often used in industry for the production of fluorescent lamps [26, 27]. If the degree of substitution is very small (<2%), the Ca2 positions will preferably be substituted. This is accompanied by the loss of PO_4^{3-} ions, so the crystal lattice will compensate for the charge imbalance in this way. However, when the degree of change is higher, the replacement of Ca^{2+} with trivalent ions is accompanied by the substitution of F^- with divalent cations and / or the substitution of Ca^{2+} with a monovalent anion. Specifically, the exchange mechanism is 2Sb^{3+} for 3 adjacent Ca^{2+} at the Ca1 position.

Rare earth ions (REE^{3+}) can make substitutions in both cationic positions Ca1 and Ca2 [28]. In general, the most frequently tested Eu^{3+} cation will replace the FAP lattice in the Ca2 position with F substitutions with O^{2-} anions due to the charge balance, but also the possible creation of a vacancy (F_2n^-) [29]. In the case of Pr^{3+} substitutions, it has been observed that they have an affinity for the Ca2 position and that there are substitutions of F^- with O^{2-} anions due to the charge balance, but also the possible creation of a vacancy [18].

In the case of co-doped FAP, by the $\text{Yb}^{3+}/\text{Ho}^{3+}$ cation system, it was assumed that there were 13Yb^{3+} and 2Ho^{3+} in 10 unit cells [30]. The charge balance is achieved by forming a vacancy at the Ca^{2+} position, as well as by substituting F with O^{2-} .

Conclusion

New types of biomaterials for a wide range of biomedical applications have been obtained by substitutions of different metals in the crystal matrix of fluorapatite. The crystal lattice of fluorapatite is tolerant to various isomorphous substitutions. When replacing Ca ions with metals, a widespread phenomenon is coupled substitution, when anions are also replaced in order to preserve the neutrality of the lattice. In addition to these structural properties, doped metals affect both the luminescent and biological properties of fluorapatite materials.

Acknowledgments

The authors are grateful to the Ministry of Education, Science and Technological Development of the Republic of Serbia (Contract number: 451-03-9/2021-14/200023) for the financial support.

References

1. D. Milojkov, Dobijanje nanofosfora na bazi fluorapatita dopirani Pr³⁺ jonima za bio-medicinske primene, Doktorska disertacija, Tehnološki fakultet Novi Sad, Univerzitet u Novom Sadu, 2020.
2. Q. Fan, X. Cui, H. Guo, Y. Xu, G. Zhang, B. Peng, Application of rare earth-doped nanoparticles in biological imaging and tumor treatment, *Journal of Biomaterials Applications* 35(2) 2020, 55-70.
3. V. Stanić, S. Dimitrijević, D. G. Antonović, B. M. Jokić, S. P. Zec, S. T. Tanasković, S. Raičević, Synthesis of fluorine substituted hydroxyapatite nanopowders and application of the central composite design for determination of its antimicrobial effects, *Applied Surface Science*, 290 (2014) 346–352
4. V. Stanić, A. S. Radosavljević-Mihajlović, V. Živković-Radovanović, B. Nastasijević, M. Marinović-Cincović, J. P. Marković, M. D. Budimir, Synthesis, structural characterisation and antibacterial activity of Ag⁺-doped fluorapatite nanomaterials prepared by neutralization method, *Applied Surface Science*, 337 (2015) 72–80
5. T. Shalika, H. Perera, Y. Han, X. Lu, X. Wang, H. Dai, S. Li, Rare Earth Doped Apatite Nanomaterials for Biological Application, *Journal of Nanomaterials*, Vol. 2015, Article ID 705390, 6 pages, 2015.
6. K. Hasna, S. Sasanka Kumar, M. Komath, M. Raama Varma, M. K. Jayaraj, K. Rajeev Kumar, Synthesis of chemically pure, luminescent Eu³⁺ doped HAp nanoparticles: a promising fluorescent probe for in vivo imaging applications, *Phys. Chem. Chem. Phys.*, 15 (2013) 8106—8111
7. P. Sobierajska, R. Pazik, K. Zawisza, G. Renaudin, J. Nedelec, R. J. Wiglusz, Effect of lithium substitution on the charge compensation, structural and luminescence properties of nanocrystalline Ca₁₀(PO₄)₆F₂ activated with Eu³⁺ ions, *CrystEngComm*, 18 (2016) 3447–3455
8. X. Li, J. Zhu, Z. Man, Y. Ao, H. Chen, Investigation on the structure and upconversion fluorescence of Yb³⁺/Ho³⁺ co-doped fluorapatite crystals for potential biomedical applications, *nature, SCIENTIFIC REPORTS* | 4 : 4446 | DOI: 10.1038/srep04446
9. D. Ekendahl, L. Judas, L. Sukupova, OSL and TL retrospective dosimetry with a fluorapatite glass-ceramic used for dental restorations, *Radiation Measurements*, 58 (2013) 138-144
10. M. E. Fleet, Y. Pan, Site preference of rare earth elements in fluorapatite, *American Mineralogist*, 80 (1995) 329-335
11. M. Xie, R. Pan, Photoluminescence and Ce³⁺ → Tb³⁺ energy transfer in fluoro-apatite host Ca₆La₂Na₂(PO₄)₆F₂, *Optical Materials*, 35 (2013) 1162–1166
12. P. D. Bhoyar, S. J. Dhoble, Analysis of electron–vibrational interaction in interconfigurational 5d→4f transition of Eu²⁺ ions in Na₅Ca₄(PO₄)₄F, *Luminescence*, 31 (2016) 1414–1418
13. Y. Liu, C. Yu, W. Zhang, J. Li, B. Peng, W. Wei, Synthesis and properties of Eu³⁺-doped strontium fluoroapatite nanocrystals by low-temperature hydrothermal method, *OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS V*, 4 (2010) 445 – 448
14. J. C. Elliott, Structure and chemistry of the apatites and other calcium orthophosphates, *ELSEVIER SCIENCE B.V.*, P.O. Box 211,1000 AE Amsterdam, The Netherlands, 1994.
15. J.M. Hughes, J. Rakovan, The crystal structure of apatite, Ca₅(PO₄)₃(F,OH,Cl). *Phosphates: Geochemical, Geobiological, and Materials Importance*, 48 (2002) 1–12

16. Lj. Veselinović, Redgenska analiza nanostrukturnih prahova kalcijum fosfata dobijenih novim postupcima sinteze, Magistarska teza, Univerzitet u Beogradu, Rudarsko-geološki fakultet, 2010.
17. N. Leroy, E. Bres, Structure and substitutions in fluorapatite, *European Cells and Materials*, 2 (2001) 36-48.
18. Milojkov, D.V.; Silvestre, O.F.; Stanić, V.D.; Janjić, G.V.; Mutavdžić, D.R.; Milanović, M.; Nieder, J.B. Fabrication and characterization of luminescent Pr³⁺ doped fluorapatite nanocrystals as bioimaging contrast agents. *J. Lumin.* 2020, 217, 116757.
19. Milojkov, D.V.; Stanić, V.; Dimović, S.; Mutavdžić, D.R.; Živković-Radovanović, V.; Janjić, G.V.; Radotić, K. Effects of Ag⁺ ion doping on UV radiation absorption and luminescence profiles of fluorapatite nanomaterials obtained by neutralization method. *Acta Phys. Pol., A* 2019, 136, 86-91.
20. D. V. Milojkov, M. Milanović, V. M. Vasić, D. R. Mutavdžić, G. V. Janjić, B. J. Nastasijević, V. Stanić, Luminescent fluorapatite nanomaterials for biomedical applications, 4th Annual Action Conference Optical Nanospectroscopy IV, Lisbon, 2017.
21. E.R. Kreidler, F.A. Hummel, The crystal chemistry of apatite: structure fields of fluor- and chlorapatite. *Am. Miner.* 55 (1970) 170-184.
22. J. C. Elliott, Structure and chemistry of the apatites and other calcium orthophosphates, Elsevier Science B.V., AE Amsterdam, 1994.
23. J.M. Hughes, M. Cameron, K.D. Crowley, Ordering of divalent cations in the apatite structure :Crystal structure refinements of natural Mn- and Sr-bearing apatite. *Am. Miner.* 76 (1991) 1857-1862.
24. M. Miyake, K. Ishigaki, T. Suzuki, Structure refinements of Pb²⁺ ion-exchanged apatites by X-ray powder pattern-fitting, *J. Solid State Chem.* 61 (1986) 230-235.
25. A. Nounah, J.L. Lacout, Localization of cadmium containing hydroxy- and fluorapatites. *J Al Com.* 188 (1992) 141-146.
26. B.G. DeBoer, A. Sakthivel, J.R. Cagle, R.A. Young, Determination of the Antimony Substitution Site in Calcium Fluorapatite from Powder X-ray Diffraction Data, *Acta. Cryst. B* 47(1991) 683-692.
27. P.E. Mackie, R.A. Young, Location of Nd dopant in Fluorapatite, Ca₅(PO₄)₃F:Nd, *J. Appl. Cryst.* 6 (1973) 26-31.
28. M. E. Fleet, Y. Pan, Site preference of rare earth elements in fluorapatite, *Am. Miner.* 80 (1995) 329-335.
29. R. Shao, S.K. Bhattacharya, R. Debnath, A new type of charge compensating mechanism in Ca₅(PO₄)₃F:Eu³⁺ phosphor, *J. Solid State Chem.* 175 (2003) 218-225
30. Hu, X.; Zhu, J.; Li, X.; Zhang, X.; Meng, Q.; Yuan, L.; Zhang, J.; Fu, X.; Duan, X.; Chen, H.; Ao, Y. Dextran-coated fluorapatite crystals doped with Yb³⁺/Ho³⁺ for labeling and tracking chondrogenic differentiation of bone marrow mesenchymal stem cells in vitro and in vivo. *Biomaterials* 2015, 52, 441-451.