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STRUCTURA CRISTALINĂ ȘI PROPRIETĂȚI FOTOLUMINESCENTE ALE
[Nd(NO₃)₃(H₂O)₄](iso-C₉H₆N₆)₂(H₂O)

CRYSTAL STRUCTURE AND PHOTOLUMINESCENCE PROPERTIES OF
[Nd(NO₃)₃(H₂O)₄](iso-C₉H₆N₆)₂(H₂O)

Victor Krațov, dr, conf. cerc., Institutul de Fizica Aplicată, Universitatea de Stat din Moldova
Nikita Siminel, cerc., Institutul de Fizica Aplicată, Universitatea de Stat din Moldova
Marina Fonari, dr, conf. cerc., Institutul de Fizica Aplicată, Universitatea de Stat din Moldova
Elena Lucenti, dr, Institute of Chemical Sciences and Technologies "Giulio Natta", Milano, Italy

Victor Kravtsov, PhD, Institute of Applied Physics, Moldova State University
ORCID:0000-0002-1955-8480

Nikita Siminel, Institute of Applied Physics, Moldova State University
ORCID:0000-0002-1055-7078

Marina Fonari, PhD, Institute of Applied Physics, Moldova State University
ORCID:0000-0002-2508-5368 fonari.xray@gmail.com

Elena Lucenti, PhD, Institute of Chemical Sciences and Technologies "Giulio Natta", Milano, Italy
ORCID:0000-0002-2418-7565

Rezumat. Structura cristalului și proprietățile de emisie bazate pe liganzi sunt raportate pentru compusul de incluziune [Nd(NO₃)₃(H₂O)₄](iso-C₉H₆N₆)₂(H₂O), unde iso-C₉H₆N₆=triimidazo[1,2-a:1',2'-c:1'',5''-e][1,3,5]triazine.

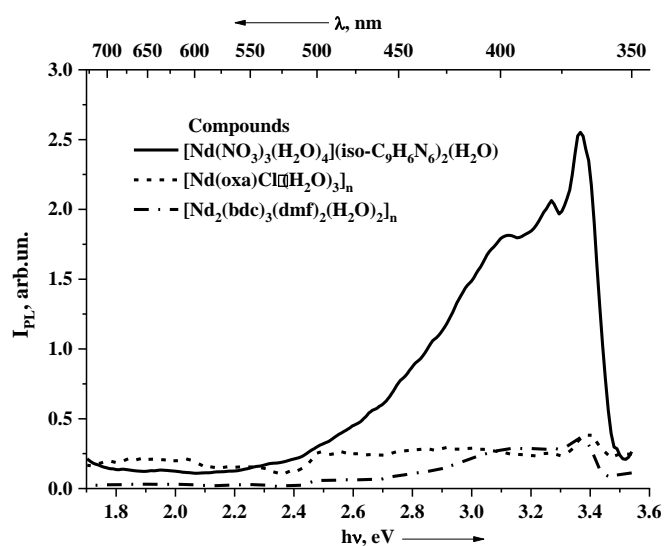
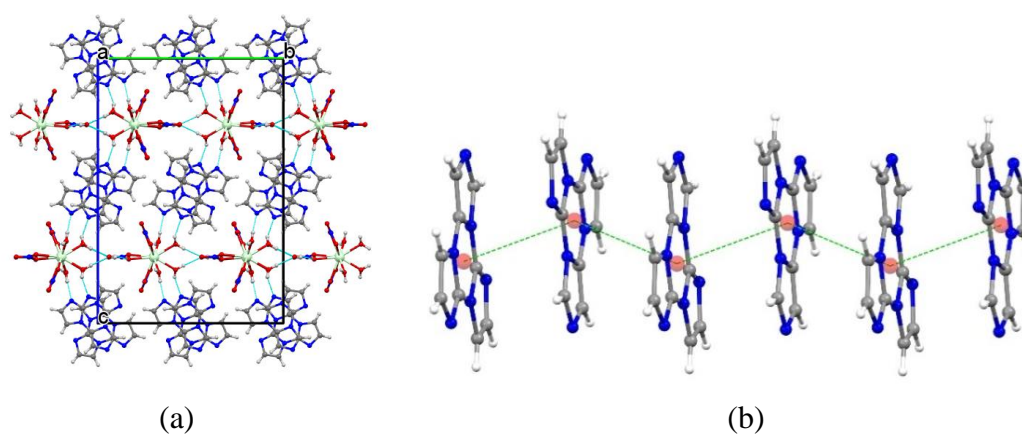
Cuvinte cheie: raze X, fotoluminescență, fluorofor organic.

Abstract. Crystal structure and ligand-based emission properties are reported for inclusion compound [Nd(NO₃)₃(H₂O)₄](iso-C₉H₆N₆)₂(H₂O), where iso-C₉H₆N₆=triimidazo[1,2-a:1',2'-c:1'',5''-e][1,3,5]triazine.

Keywords: X-ray, photoluminescence, organic fluorophore

The Nd(III)-containing systems emitting in the near-infrared (NIR, 800-1700 nm) region receive much attention due to their line-like emission spectra and high-luminescence quantum efficiency. These systems are considered as useful infrared luminescent materials for application in laser systems (1064 nm laser) and for in vivo disease diagnostics due to the relative transparency of human tissue at approximately 1000 nm. However, the emission intensity strongly depends on the organic phosphor which, if coordinated to Nd(III), protects metal ions from vibrational coupling and increases the light absorption cross section by "antenna effects" [1]. The previous research revealed meaningful emission properties for two cyclic triimidazoles, triimidazo[1,2-a:1',2'-c:1'',2''-e][1,3,5]-triazine (C₉H₆N₆), and its positional isomer, triimidazo[1,2-a:1',2'-c:1'',5''-e][1,3,5]triazine) (iso-C₉H₆N₆) [2]. Both chromophores demonstrated excellent coordinating abilities with Cu(II), Zn(II) and Cd(II) [3,4]. Here we report on the interaction of Nd(NO₃)₃·6H₂O with iso-C₉H₆N₆ resulting in partial replacement of water molecules by chromophore and its inclusion in the matrix of inorganic salt crystal with the formation of H-bonded adduct. Compound [Nd(NO₃)₃(H₂O)₄](iso-C₉H₆N₆)₂(H₂O) crystallizes in the orthorhombic *Pbcn* space group, *a*=6.7312(3), *b*=17.6785(8), *c*=25.2085(16) Å, *V*= 2999.8(3) Å³, *Z*=4. The mononuclear inorganic complex [Nd(NO₃)₃(H₂O)₄]

occupies position on the two-fold axis with Nd atom in O₁₀ coordination environment provided by three bidentate-chelate nitrate-groups and four water molecules. The Nd-O distances are in the range 2.410(4)-2.641(4) Å. The complexes are associated in the H-bonded layer parallel to the *ab* plane through OH...O hydrogen bonds with participation of coordinated and outer-sphere water molecules and nitrate-groups. Along the *c*-axis the inorganic layers are separated by the rows of iso-C₉H₆N₆ chromophores that attach to the inorganic layers through OH...N hydrogen bonds and form stacking columns (Fig. 1a). Inside the columns chromophore molecules show significant overlap with the alternating rather short separations of 3.647 and 3.668 Å between the centroids of organic molecules (Fig. 1b). No short contacts between the iso-C₉H₆N₆ columns were registered. The lack of direct Nd(III)-N(iso-C₉H₆N₆) coordination resulted in the absence of antenna effect, while the irradiation of sample by Excitation YAG:Nd³⁺ laser (λ=355 nm, room temperature) allowed to register the emission specific for the pure phase of iso-C₉H₆N₆ chromophore (Fig. 1c) [2]. For comparison, no notable emission was registered in the same experimental conditions for [Nd(oxa)Cl(H₂O)₃]_n (oxa=oxalate) and [Nd₂(bdc)₃(dmf)₂(H₂O)₂]_n (bdc=1,4-benzenedicarboxylate) [5].



(c)

Fig. 1. (a) Crystal packing in [Nd(NO₃)₃(H₂O)₄](iso-C₉H₆N₆)₂(H₂O) with indication of hydrogen bonds. (b) The column of stacked ligands. (c) Emission spectra for [Nd(NO₃)₃(H₂O)₄](iso-C₉H₆N₆)₂(H₂O) (solid line), [Nd(oxa)Cl(H₂O)₃]_n (dashed line) and [Nd₂(bdc)₃(dmf)₂(H₂O)₂]_n (dash-dotted line)

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