

Phosphate(III)-tetrahedra, NaO_6^- and ScO_6^- octahedra together form a (3, 6)-connected net. Thermochemical property studies show that during heating hydrogen and water are released while part of the phosphate(III) groups are oxidized to phosphate(V). $\text{Sc}[\text{PO}_3]_3$ is formed as the main crystalline decomposition product. $\text{NaSc}_3[\text{HPO}_3]_2[\text{HPO}_2(\text{OH})]_6$ represents the first example containing scandium within the family of M^mM^m metal phosphates(III). The replacement of phosphate(V) tetrahedra by phosphate(III) groups leads to a reduction of M–O–P connections, resulting in more open frameworks.[2]

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Keywords: scandium, phosphate(III), thermal analysis

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Effect of magnesium on the thermal stability of the hydroxyfluorapatite

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The biological apatite contains minor substituents such as F^- , Cl^- , CO_3^{2-} , SiO_4^{4-} , Na^+ , K^+ , Sr^{2+} , Zn^{2+} and Mg^{2+} . Therefore, the incorporation of such ions into the synthetic hydroxyapatite would enhance its biocompatibility and bioactivity. Magnesium and fluoride co-substituted hydroxyapatites with the general formula $\text{Ca}_9\text{Mg}(\text{PO}_4)_6(\text{OH})_{2-2y}\text{F}_y$ ($y = 0, 0.5, 1, 1.5$ and 2) have been synthesized through a hydrothermal method. The obtained powders have been characterized using different analyses. The results showed that the substitution of F^- for OH^- was continuous between the limiting compositions $\text{Ca}_9\text{Mg}(\text{PO}_4)_6(\text{OH})_2$ and $\text{Ca}_9\text{Mg}(\text{PO}_4)_6\text{F}_2$. Indeed, no secondary phases were formed. Furthermore, the incorporation of Mg into the hydroxyfluorapatite lattice influenced considerably its thermal behavior by lowering its decomposition temperature with respect to the nonsubstituted HFA. Also, the nature of the decomposition products tightly depended on the fluorine content. The Fullprof program was used to determine the phase distribution for the powders calcined at different temperatures. The obtained results showed that the amounts of the decomposition products increased with the increase of the calcination temperature. According to the nature of the decomposition products, it seems that the MHF_yA samples exhibit a thermal behavior similar to that of MHA rather than that of MFA.

Keywords: apatite, magnesium

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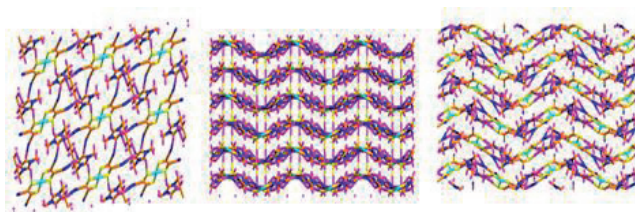
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Role of supramolecular interactions on electronic absorption spectra of metal dithiolene complexes

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Metal-maleonitriledithiolate (mnt) complexes have received considerable attention in the areas of conducting and magnetic materials, dyes, non-linear optics, and catalysis [1]. Typically, the geometry around the transition metal ions (Cu, Ni) possesses square-planar arrangement, and in case of Mn, Fe, Co-mnt complexes, the geometry is noticeably distorted square-planar [2]. We describe here a series of highly distorted

square-planar ion-pair complexes in which $[\text{M}(\text{mnt})_2]^{2-}$ ($\text{M} = \text{Cu}, \text{Ni}$) anions are associated with alkyl imidazolium cations of varied alkyl chain lengths. In the present study, a systematic study of variation of square planar geometries (in terms of distortion) around the metal ion in customary square planar metal-dithiolene complexes has been discussed. This distortion in the geometry around the metal ion can be ascribed due to un-balanced supramolecular interactions, that include $\text{S}\cdots\text{H}$, $\text{N}\cdots\text{H}$ and $\text{M}\cdots\text{S}$ type of weak contacts. The title complexes show a moderate absorption band in the NIR region at 1210 nm and 800 nm, in their solution states for the copper and nickel dithiolene ion-pair complexes respectively. The absorption maxima in the solid-state diffuse reflectance spectra is mainly depends on the geometry around the copper metal, e.g., the square planar copper-dithiolene complexes exhibit broad band at 1150 nm whereas distorted square planar ($\lambda = 38.31^\circ$) copper-dithiolene complexes show a broad band at 1260 nm, indicating a bathochromic for the more distorted square planar copper complexes. All the compounds are unambiguously characterized by single crystal X-ray crystallography, and further characterized by IR, ^1H NMR, LCMS, EPR spectral- and electrochemical-studies.



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Keywords: supramolecular interactions, diffuse reflectance spectra.

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Crystal structure and phase transition of $\text{Rb}_{1-x}(\text{NH}_4)_x\text{IO}_3$ mixed crystal

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Ammonium iodate, NH_4IO_3 , is a well known electro-optic material [1] and exhibits a strong piezoelectric effect [2]. Ferroelectricity was reported at 1975 with a transition temperature to paraelectric phase near 85°C [3]. In Rubidium iodate, RbIO_3 , there is no report of the existence of ferroelectricity and phase transition. On the other hand, Potassium iodate, KIO_3 , is known as successive phase transition within ferroelectricity [4]. Therefore, it is strange that RbIO_3 does not undergo the phase transition, like as KIO_3 or NH_4IO_3 . In order to clarify this question, we carried out the measurement of differential scanning calorimetry and the experiment of powder X-ray diffraction of $\text{Rb}_{1-x}(\text{NH}_4)_x\text{IO}_3$ with $x=0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0$.

According to the results, the following things have become clear now. In all compositions of x , $\text{Rb}_{1-x}(\text{NH}_4)_x\text{IO}_3$ mixed crystals were the single crystalline solid solution. The crystal structure of $x=0.1, 0.2$ and 0.3 was approximately-same crystal structure of RbIO_3 , and one

of $x=0.7$, 0.8 and 0.9 was almost same one of NH_4IO_3 . Meanwhile, the crystal structure of the middle compositions ($x=0.4$, 0.5 and 0.6) was different from both of RbIO_3 and NH_4IO_3 .

The measurement of DSC in temperature range from room temperature to 135°C , $\text{Rb}_{1-x}(\text{NH}_4)_x\text{IO}_3$ with $x=0.0$ to 0.6 indicate no anomaly. However, single anomaly in DSC measurement was observed in the each sample of $x=0.7$ to 1.0. From a reported temperature of ferroelectric phase transition in NH_4IO_3 [3], it was considered that these DSC anomalous temperatures were equivalent to temperature of the ferroelectric phase transition. These temperatures of ferroelectric phase transition were decreased with decreasing the value of composition x from $x=1.0$ to $x=0.7$. The values of the entropy change at the ferroelectric phase transition of $x=0.8$, 0.9 and 1.0 were obtained from the value of these heat anomaly in DSC measurement of each samples. As a result, it was considered these ferroelectric phase transition was an order-disorder type.

Now, we are carrying out the low temperature DCS measurement and the identification of the crystal structure of middle composition region ($x=0.4$, 0.5 and 0.6). In congress, we will show the crystal structures and DSC measurements, and will discuss the phase diagram and the mechanism of phase transition in $\text{Rb}_{1-x}(\text{NH}_4)_x\text{IO}_3$ mixed crystals.

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Keywords: rubidium ammonium iodate mixed crystal, X-ray diffraction, differential scanning measurement

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New molybdenum peroxocomplexes as a promising catalysts

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Molybdenum organometallic complexes and oxides catalyze epoxidation reactions in homogenous and heterogenous catalysis. In addition, molybdenum complexes, in particular peroxomolybdates show structural and functional analogy to enzymes containing Mo atom, therefore are active in various reactions [1]. Most of the molybdenum catalysts play an important role in environment protection. They are used in desulphurization of petroleum and coal derived products, as sulphur dioxide causes a serious deterioration of air quality [2].

In our laboratory almost a dozen of a new peroxomolybdates have been obtained, they have been thoroughly investigated by X-ray and spectroscopic methods [3]. Recently, three new peroxocomplexes were synthesized from ammonium molybdate solution with addition of nicotinic acid and hydrogen peroxide (compounds **I-III**, see Table 1). In Figure 1a) anion coordination polyhedron and in 1b) asymmetric unit of peroxocomplex **I** are presented. The molybdenum atom is coordinated by seven oxygen atoms, among them there are two peroxo-groups lying in the same plane, one terminal O atom and two bridging oxygen atoms. Compound **I** is an ammonium salt, compound **II** is a salt of the same acid with protonated nicotinic acid. In Table 1 summary of crystal data of new peroxo-molybdenum complexes are presented.

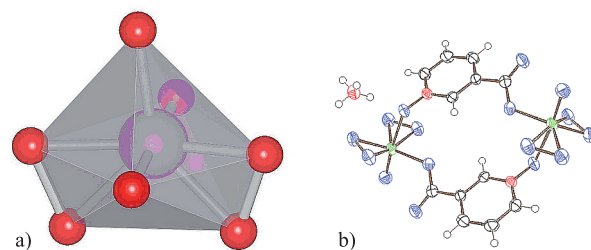


Figure 1, a) Anion coordination polyhedron and b) asymmetric unit of compound **I** (Mo-green, O-blue, N-red, C-grey).

Table 1. Crystal data of new peroxo-molybdates with nicotinic acid.

Chemical formula	$\text{C}_{12}\text{H}_{18}\text{Mo}_2\text{N}_4\text{O}_{16}$ I	$\text{C}_{24}\text{H}_{22}\text{Mo}_2\text{N}_4\text{O}_{22}$ II	$\text{C}_{12}\text{H}_{12}\text{Mo}_2\text{N}_2\text{O}_{16}$ III
SG	P-1 (2)	$P2_1/c$ (14)	Pc (7)
Cell parameters [\AA , $^\circ$]	a=6.687(4) b=6.965(4) c=12.012(7) $\alpha=76.421(4)$ $\beta=77.434(4)$ $\gamma=69.478(4)$	a=7.504(2) b=28.473(7) c=7.777(2) $\beta=111.425(1)$	a = 5.416(3) b = 5.350(2) c = 16.976(7) $\beta = 106.230(3)$
V [\AA^3], Z	503.66(2), 1	1546.82(3), 2	472.29(4), 2
R1; wR2	0.0422; 0.0902	0.0282; 0.0622	0.0508; 0.1342

Some peroxo-nicotinic acid complexes of Mo, have been investigated by Djordjevic et al., [4], their samples were not investigated by X-ray methods, but with the use of chem. analysis, spectroscopic, ^1H and ^{13}C NMR studies they proposed structures which differ from ours.

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Indialite and cordierite in glass ceramics for millimeterwave dielectrics

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Dielectrics for millimeterwave communications are expected to have low dielectric constant and high quality factor (high Q). Cordierite ceramics is a candidate for millimeterwave dielectrics, because of low dielectric constant 4.7, and high Q f more than 200,000 GHz. Cordierite has two polymorphs: disordered phase indialite (hexagonal, $P6/mcc$ (No. 192)) and ordered phase cordierite (orthorhombic, $Cccm$ (No.66)). As Ni-doped cordierite ceramics with good dielectric properties tend to disordered, indialite was expected to have high Q f. As indialite