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Nowadays polydisperse titanium dioxide (TiO<sub>2</sub>) is one of the most popular investigated object among metal oxides due to its wide applications.

TiO<sub>2</sub> materials of a high chemical purity, as-prepared and modified by metal cations (Fe<sup>3+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>), have been investigated by the X-ray diffraction, X-ray fluorescence and AFM methods. All TiO<sub>2</sub> powders have a fine-dispersated anatase structure and consist of grown together nanocrystallites of ~ 8 – 17 nm. TiO<sub>2</sub> particles, usually ranging from 100 to 600 nm, show the ability to form large agglomerates, up to 2 μm in size. Contrary to pure anatase, metal-modified TiO<sub>2</sub> particles possess a positive charge on their surface and can be lifted away by the AFM tip from the substrate surface during the scanning. The strength of interactions between the AFM silicon tip and TiO<sub>2</sub> powders is different for each sample. In particular, the AFM tip removes Fe/A300 particles up to 250 nm in diameter, Co/A300 – 180 nm, Cu/A300 – 120 nm. The possible interaction mechanisms between different TiO<sub>2</sub> particles and the silicon tip are discussed. The electrostatic force has been found to play an essential role in the sample – tip interaction processes, and its value depends on the type of metal cation used.

**Keywords:** structural analysis, AFM, inorganic oxides

#### P.08.14.2

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#### Structural Conditionality of Physical Properties in Nb or Sb Doped KTP Crystals

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KTiOPO<sub>4</sub> (KTP) crystals and their solid solutions attract researchers attention by nonlinear optical characteristics. High ionic conductivity and ferroelectric phase transition of these crystals are also of great interest. All of these properties are susceptible to the changing of the crystals composition and can be regulated within certain limits by means of isomorphic replacements. Two series of KTP single crystals (sp.gr. Pna2<sub>1</sub>) doped with Nb and Sb were grown. Features of physical properties and atomic structure of five crystals doped with Nb and three crystals doped with Sb were studied. For single crystals K<sub>1-x</sub>Ti<sub>1-x</sub>Nb<sub>x</sub>OPO<sub>4</sub> (KTP:Nb) и K<sub>1-x</sub>Ti<sub>1-x</sub>Sb<sub>x</sub>OPO<sub>4</sub> (KTP:Sb) the maximal x values are 0.11 and 0.23 correspondingly. New additional positions of K cations and a lot of potassium vacancies were found in the structure of KTP:Nb and KTP:Sb crystals. X-ray structural study of K<sub>0.93</sub>Ti<sub>0.93</sub>Nb<sub>0.07</sub>OPO<sub>4</sub> crystal at 30K was done in order to localize safely the additional K positions with low occupancy. Results of this structural study confirmed the model received at room temperature and allowed establishing of presence of the potassium positions removal along c axis, which depends on temperature. Decreasing of the temperature of ferroelectric phase transition and strengthening of relaxation effect in the doped crystals are concerned with displacement and splitting of potassium positions. Disorder in the potassium sub-lattice leads to the increase of conductivity.

**Keywords:** structure physical property relationships, superionic conductivity, nonlinear optical materials

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#### Lanthanides Stereochemistry in the Structure of Oxygen Containing Compounds

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The crystallographic analysis of 3476 compounds containing 4044 coordination polyhedrons LnO<sub>n</sub> (Ln = La – Lu) has been carried out (data have been taken from [1] and [2]). Coordination numbers (CN) of all atoms, coordinates of missing hydrogen atoms and characteristics of Voronoi-Dirichlet polyhedrons (VDP) of Ln atoms have been calculated by means of program complex TOPOS [3]. It

was found out that CN(Ln) changes from 3 to 12, growth of CN is accompanied by increase of r(Ln-O) but VDP volume (V<sub>VDP</sub>) of Ln atom depends only on Ln nature and its oxidation state. In our opinion this fact may be an evidence of a viewpoint in which complexing atom should be described as soft (that is able for deformation) sphere with a volume equal to V<sub>VDP</sub> (radius of the sphere is R<sub>SD</sub>). It was established that R<sub>SD</sub>(Ln<sup>3+</sup>) meanings reduce from La to Lu. Decrease of oxidation state of Ln atom is corresponded by growth of their VDP volumes on 1 – 4 Å<sup>3</sup>. It was shown that the VDP characteristics may be used for determination of oxidation state of Ln atoms in crystal structure, description and analysis of nonvalent (for example agostic Ln...H-C) interactions and bonds between two metal atoms.

[1] *Inorganic crystal structure database, Release 2002/1*, FIZ Karlsruhe & NIST Gaithersburg, 2002. [2] *Cambridge structural database system, Version 5/25*, Cambridge Crystallographic Data Centre, 2003. [3] Blatov V.A., Shevchenko A.P., Serezhkin V.N., *J. Appl. Cryst.*, 1999, **32**, 377.

**Keywords:** lanthanides, computational analysis of crystallographic data, Voronoi-Dirichlet polyhedron

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#### Counteranion Effect on Macrocyclic Complex Materials

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Dinuclear copper (II) macrocyclic complexes derived from the condensation of 4-methyl-2,6-diformylphenol with 1,3-diamine-2-propanol, with different counteranions, [Cu<sub>2</sub>LCl<sub>2</sub>]-2H<sub>2</sub>O **1**; {[Cu<sub>2</sub>L(μ<sub>2</sub>-acetate)](acetate) **2a** [Cu<sub>2</sub>L(acetate)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] **2b** }·6H<sub>2</sub>O; [Cu<sub>2</sub>L(H<sub>2</sub>O)<sub>2</sub>](SO<sub>4</sub>H)-2H<sub>2</sub>O **3**, have been prepared. **1** and **3** crystallize in the triclinic P  $\bar{1}$  (#2) space group with a=7.7223(16), b=9.3901(19), c=10.167(2) Å; α=73.377(3)β=85.768(4), γ=65.766(3) °; V=643.4(2) Å<sup>3</sup>; Z=1 and a=7.727(5), b=8.663(4), c=11.753(4) Å; α=82.199(6)β=85.519(10), γ=75.830(11) °; V=754.8(7) Å<sup>3</sup>; Z=1 respectively. **2a**, **2b** co-crystallize in the orthorhombic crystal system, Pnma(#62) space group with a=15.1671(11), b=27.4366(19), c=15.9786(11) Å; V=6649.2(8) Å<sup>3</sup>; Z=4. The copper (II) ions present a square base pyramidal geometry in three of the reported complexes, with axially coordinated halogens **1**, a syn-syn acetate ligand **2b** and water molecules **3**. Compound **2a** can be described as having a distorted octahedral environment, with aqua and acetate oxygens in the apices. Compound **2b** which co-crystallized with **2a**, presents a folded structure of the macrocyclic ligand due to the presence of the bridging acetate molecule. Strong antiferromagnetic exchange is observed in all complexes. The correlation between magnetic properties and structure will be discussed.

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**Keywords:** copper, macrocycles, magnetic materials

#### P.08.14.5

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#### Hybrid Organo-inorganic Materials of the VPO System

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One of the methods to obtain materials based on the VPO system is to incorporate organic molecules that modify the oxide structure. The organic species can be introduced as simple cationic species which act as charge compensating agents, or as the ligand of a transition metal complex species. Here we report the synthesis of [Cu<sub>2</sub>L<sub>2</sub>(VO<sub>2</sub>)(HPO<sub>4</sub>)<sub>2</sub>NO<sub>3</sub>]<sub>n</sub> where L=bipy (**1**), phen (**2**) and the corresponding magneto-structural characterization. (**1**) and (**2**) crystallize in the P-1 space group with a=10.5927(13), b=12.0359(15), c=12.1655(15) Å; α=107.090(2), β=110.399(2), γ=93.876(2)°; V=1364.3(3) Å<sup>3</sup>; Z=2 for (**1**) and a=7.936(5), b=12.122(5), c=16.066(5) Å; α=107.216(5), β=94.496(5), γ=100.390(5)°;

$V=1437.7(3)\text{\AA}^3$ ;  $Z=2$  for (2). The copper(II) ions present a square base pyramidal geometry in these reported complexes with a Cu-Cu distance of 5.013 and 5.017 Å for (1) and (2) respectively. Both compounds present antiferromagnetic behaviour with  $T_m$  of 15.5 and 32 K for (1) and (2). The magnetic behaviour will be compared with other reported Cu-VPO systems.<sup>1</sup>

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[1] Moreno Y., Vega A., Ushak S., Baggio R., Peña O., Le Fur E., Pivan J.Y., Spodine E., *J. Mater. Chem.*, 2003, **13**, 2381.

**Keywords:** magnetic materials, copper, VPO system

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#### Partial Phase Diagram of Pd-Mn System Studied by Electron Diffraction and Microscopy

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Among ordered phases reported in the present alloy system, four of Pd<sub>3</sub>Mn (or Pd<sub>3</sub>Mn II), Pd<sub>2</sub>Mn, Pd<sub>5</sub>Mn<sub>3</sub> and PdMn were confirmed to be stable, but no indications of Pd<sub>3</sub>Mn I and Pd<sub>21</sub>Mn<sub>11</sub> were obtained.

In the solid solution range from 25 to 50at%Mn, the crystal structure continuously transforms from D0<sub>23</sub> type to L1<sub>0</sub> type with increasing Mn content. The magnitude of  $c_0/a_0$  of the basal lattice is 1.0 for 25.0-26.5at%Mn, and then decreases down to 0.91 at 36.1at%Mn. The Pd<sub>3</sub>Mn phase is defined in the range from 25.0 to 26.5at%Mn, because  $c_0/a_0=1.0$  in this range is the characteristic of D0<sub>23</sub> type structure. The electron micrograph shows the arrangement of minority atoms (Mn) in D0<sub>23</sub> type. For Mn content more than 37at%, the PdMn phase with L1<sub>0</sub> type is stable above 600°C. In the compositions between Pd<sub>3</sub>Mn and PdMn phases, the occupation probability of Mn at each atom-site was expressed in terms of alloy composition.

The Pd<sub>2</sub>Mn phase is stable below 700°C. The electron micrograph shows the arrangement of Mn atoms, which supports the structural model reported already [1]. The Pd<sub>5</sub>Mn<sub>3</sub> phase was confirmed by electron diffraction patterns with different incidences. This phase is ranked as the second ordered structure of the PdMn phase. On the basis of ordered structures confirmed there, a partial phase diagram was proposed for Pd-rich Pd-Mn alloys.

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**Keywords:** electron diffraction, ordered structures, phase diagrams

#### P.08.14.7

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#### Crystal Structure of $\beta$ -KU<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> – a Member of the Group with NZP Structure Type

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The study of synthetic double Potassium-Uranium orthophosphate KU<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> is part of a program on the crystal chemistry of double orthophosphates with general formula (M1)<sub>0→1</sub>(M2)<sub>0→3</sub>{[L<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>]<sup>P</sup>}<sub>3z</sub>, where (M1)<sub>0→1</sub> and (M2)<sub>0→3</sub> are types of extraframework cation positions in holes with the indications of position numbers and L is the framework position, that includes determination of phases obtained by sol-gel technique. The NaZr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (NZP) structural type [1] is widely distributed among them. The distinguishing characteristic feature of the NZP structure is that the same crystallographic positions in this structure can accommodate elements, both small and large, in oxidation states from +1 to +5 with retention of the principal framework. In this work the compound  $\beta$ -KU<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> was recently studied by x-ray powder diffraction and Rietved method in space group R-3c. The synthesis of new framework phosphates belonging to

the NZP structural type, as well as detailed analysis of the geometric and topological features of the structures of new and known NZP-type phosphates aimed at revealing correlations between the crystal structures of these compounds and the practically valuable physicochemical properties, have attracted considerable attention in recent years [2].

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**Keywords:** phosphates, X-ray diffraction, Rietveld method

#### P.08.14.8

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#### Transition Metal Hydroxy-Terephthalates: Structure-Magnetism Relationship

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The title compounds belong to the family of hybrid lamellar materials where transition metal ions form layers spaced by organic anions. Metal hydroxy-terephthalates M<sub>x</sub>(OH)<sub>2x-2</sub>(tp) (tp =C<sub>8</sub>H<sub>4</sub>O<sub>4</sub>, M = Zn, Mn, Fe, Co, Ni, Cu) have been synthesized by hydrothermal route and their crystallographic structures were determined. Zn<sub>3</sub>(OH)<sub>4</sub>(tp) has been characterized from X-ray single crystal diffraction data: C2/c,  $a=28.100\text{\AA}$ ,  $b=6.310\text{\AA}$ ,  $c=14.836\text{\AA}$ ,  $\beta=121.56^\circ$ . The zinc atoms exhibit tetrahedral, octahedral and bi pyramidal coordinations, forming step-like layers bridged by terephthalate moieties. As for the paramagnetic ions, the layered structures of the model compounds Co<sub>2</sub>(OH)<sub>2</sub>(tp) (C2/m,  $a=19.943\text{\AA}$ ,  $b=3.289\text{\AA}$ ,  $c=6.289\text{\AA}$ ,  $\beta=95.75^\circ$ ) [1] and Cu<sub>2</sub>(OH)<sub>2</sub>(tp) (P-1,  $a=10.143\text{\AA}$ ,  $b=6.339\text{\AA}$ ,  $c=3.484\text{\AA}$ ,  $\alpha=99.17^\circ$ ,  $\beta=95.75^\circ$ ,  $\gamma=98.76^\circ$ )[2] were determined *ab-initio* from XRPD data. The metallic cations lie in oxygen octahedra. Despite similar structures, different magnetic behaviors are observed depending on the metal ion and on symmetry differences. Low-temperature ferromagnetic-like ordering will be discussed on the basis of the structural features.

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**Keywords:** lamellar hybrid compound, transition metal, structure-properties relationship

#### P.08.14.9

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#### Structures of New Molecular Conductors Based on Functionalized Organic Donors

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Functionalized organic donors are remarkable for the ability to form hydrogen bonds of cation...cation and cation...anion types, which can effectively control the crystal architecture of molecular conductors [1]. Hydrogen bond network is well developed in the crystals of four new radical cation salts based on amide functionalized EDT-TTF donors EDT-TTF-CONH<sub>2</sub> (D1) and EDT-TTF-(CONH<sub>2</sub>)<sub>2</sub> (D2) [2].

Semiconducting  $\alpha'$ -(D1)<sub>4</sub>[FeNO(CN)<sub>5</sub>] (1),  $\alpha'$ -(D1)<sub>4</sub>[Co(CN)<sub>6</sub>] (2),  $\beta$ -(D1)<sub>6</sub>[Fe(CN)<sub>6</sub>] (3) and (D2)<sub>4</sub>[FeNO(CN)<sub>5</sub>]NB (4) salts have been prepared and characterized by X-ray single crystal diffraction experiments and band structure calculations. (D1)<sub>2</sub>-dimers or (D2)<sub>n</sub>-extended zigzag chains of donors connected through functional groups are found to be stable structural motifs in 1-4. The 1 and 2 salts are isostructural but contain anions of different charge, -2 and -3, respectively. The degree of charge transfer affects on electronic structures of the crystals that results in changing their transport properties:  $\sigma_{RT}(2)/\sigma_{RT}(1)=50$ . In the crystals 4 a superstructure with