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Nowadays polydisperse titanium dioxide (TiO₂) is one of the most popular investigated object among metal oxides due to its wide applications.

TiO₂ materials of a high chemical purity, as-prepared and modified by metal cations (Fe³⁺, Co²⁺, Cu²⁺), have been investigated by the X-ray diffraction, X-ray fluorescence and AFM methods. All TiO₂ powders have a fine-dispersated anatase structure and consist of grown together nanocrystallites of ~ 8 – 17 nm. TiO₂ 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 TiO₂ 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 TiO₂ 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 TiO₂ 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

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

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KTiOPO₄ (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. Pna2₁) 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_{1-x}Ti_{1-x}Nb_xOPO₄ (KTP:Nb) и K_{1-x}Ti_{1-x}Sb_xOPO₄ (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_{0.93}Ti_{0.93}Nb_{0.07}OPO₄ 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_n (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_{VDP}) 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_{VDP} (radius of the sphere is R_{SD}). It was established that R_{SD}(Ln³⁺) meanings reduce from La to Lu. Decrease of oxidation state of Ln atom is corresponded by growth of their VDP volumes on 1 – 4 Å³. 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, [Cu₂LCl₂]-2H₂O **1**; {[Cu₂L(μ₂-acetate)](acetate) **2a** [Cu₂L(acetate)₂(H₂O)₂] **2b** }·6H₂O; [Cu₂L(H₂O)₂](SO₄H)-2H₂O **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) Å³; 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) Å³; 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) Å³; 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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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 [Cu₂L₂(VO₂)(HPO₄)₂NO₃]_n 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)Å³; 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)°;