

HYDROGEN BONDED MOLECULAR ASSEMBLIES IN CRYSTALS AND GELS OF CHIRAL BIS(AMINO ALCOHOL) OXALAMIDES

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The research of supramolecular organisation of organic molecules into nano- or micro-dimensional assemblies is of high relevance for design of new materials for versatile applications and for understanding of the organisation of matter in general. Macroscopic manifestation of self-aggregation can result in ordered gels that include entrapped solvent molecules. It is recognised that gelation is based on self-assembly of gelators in solution, leading to supramolecular arrays of specific non-covalent interactions: hydrogen bonds, van der Waals interactions and metal coordination. It is a challenge to predict gelation on the basis of the constitutional and conformational characteristics of an organic molecule and the properties of the liquid to be gelled. Recently we have shown that chiral bis(amino acid) oxalamides represent a rare group of gelators capable to gel water and various lipophilic organic solvents (Makarevic et al., Chem. Eur. J. 2001, 7, 3328), whereas our new results are related to chiral bis(leucinol)oxalamides exhibiting gelating properties. The crystal structures of both, SS- and rac-bis(leucinol)oxalamide reveal two-dimensional hydrogen bonded networks through oxalamide and alcohol functionalities. X-ray powder diffraction was used to identify an appearance of crystalline phases in gels and xerogels of enantiomeric and racemic samples. In all cases the monoclinic crystalline phase identical to the crystals of SS-enantiomer was found. The high gelating properties of racemic compound might be related by van der Waals interactions between enantiomeric fibres of opposite chirality, whereas molecular organisation in fibres is governed by hydrogen bonds.

Keywords: HYDROGEN BONDING, AGGREGATION, GELS

SYNTHESIS AND CRYSTAL STRUCTURES OF NEW MOLECULAR CONDUCTORS WITH METAL-COMPLEX ANIONS

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New molecular conductors based on the donors bis(ethylenedithio)tetrathiafulvalene (ET) and 4,5-ethylenedithio-4,5-vinylenedithiotetrathiafulvalene (EVT) were synthesized and studied by X-ray analysis. The compounds include flat-square and cluster metal-complex anions. Molecular conductors on the basis of ET obtained using the bulk cluster $[\text{Re}_6\text{S}_8(\text{CN})_6]^{3-}$ anions are characterized by a remarkable deformation of the radical cation layers, that affects their conductivity. Besides, a great volume of the anion leads to appearing holes in the anionic layer which are filling by polar solvent molecules or artificial additions during the electro-synthesis. With the purpose of studying donors influence on the properties of conducting compounds a new $(\text{EVT})_4[\text{Pt}(\text{CN})_4]$ salt was synthesized and studied by X-ray analysis. The reasons of the difference in the electroconducting properties of the salt are discussed and compared with the analogous salts based on ET. This work was supported by the RFBR (project No. 00-03-32809).

Keywords: MOLECULAR CONDUCTORS; SYNTHESIS; CRYSTAL STRUCTURE

SYNTHESIS, PROPERTIES AND STRUCTURE OF NIOBIUM-DOPED POTASSIUM TITANIL PHOSPHATE CRYSTALS

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Crystals of the potassium-titanil phosphate family KTiOPO_4 (KTP) are characterized by ferroelectric phase transitions and also by superionic conductivity and non-linear optical properties. KTP:Nb single crystals were synthesized by the method of spontaneous crystallization from flux. As it was found, electrical conductivity of these crystals is very sensitive to the niobium content. It increases more than by order in comparison with pure KTP crystals. It was found also that Nb admixture influences over the temperature of the ferroelectric phase transition. For the X-ray structural analysis the single crystals containing 4 (I), 7 (II), 11(III), 64(IV) and 71(V) at.% Nb were selected. It was found, that crystals with 4, 7, 11 at.% Nb are orthorhombic (structure type KTP), space group $Pna2_1$. Single crystals with 64 and 71 at.% Nb - monoclinic, space group $P2/n$. All the five structures that we have studied are built by a three-dimensional framework of $(\text{Nb,Ti})\text{O}_6$ octahedron and PO_4 tetrahedron. The structures (I), (II) and (III) have channels along the *c*-axis, but in (IV) and (V) structures there are two types of channels along the diagonal direction [101]. Potassium cations are located in these channels. Conductivity enhance in all the studied crystals is connected with the vacancies appearance and the formation of new statistically occupied positions of potassium atoms. The study was supported by the Russian Foundation for Basic research, project no. 00-02-16059, 01-02-06407.

Keywords: CRYSTAL STRUCTURE, NONLINEAR OPTICAL MATERIALS, SOLID SOLUTION

THE SYNTHESIS, STRUCTURAL PECULIARITIES OF PEROVSKITE-LIKE STRONTIUM CUPRATES BASED ON B,Al,Ga,In,Cr,Pb,Mn,W,Mo AND Hg

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It has been known that superconducting perovskite-like cuprates conducting CuO_2 planes and charge-reservoir blocks (CRB). The CRB have some functions: to connect transport and charge blocks for perovskite-like structure formation, to form various structures of perovskite-like phases, to displace a block isomorphism, to form superstructure (commensurate or incommensurate), to produce donors of charge and effective to transfer charge for appearance of superconducting properties, to impose crystallochemical pressure on, to realize the peculiarities of physical properties. We report here the synthesis (solid-state reaction method, crystal structure (refinement by the Rietveld suite of programs DBWS-9411) and resistivity (measurements by the standard four-probe method from 300 down to 4.2 K) of the $(\text{M,Cu})(\text{Sr,Ln})_2(\text{Ln,Sr})\text{Cu}_2\text{O}_{8-d}$ (M-1212) and $(\text{M,Cu})(\text{Sr,Ln})_2(\text{Ln,Ce})_2\text{Cu}_2\text{O}_{10-d}$ (M-1222) phases with various M elements (M=B,Al,Ga,In,Cr,Pb- $T_{c_{\text{max}}}=50$ K, Mn, W, Mo and Hg- $T_{c_{\text{max}}}=108$ K) which occupy the charge reservoir cation sites (the M-O bond along the $\langle 100 \rangle$, $\langle hk0 \rangle$ or $\langle 110 \rangle$ directions) depending on ionic radii and formal charge of the M. A decrease of dimension of the M cation results in decrease of the M coordination number and, as a rule, in increase of superstoichiometric oxygen content (*d* value). It is accompanied by a change of the Cu formal charges (FC Cu). The non-optimal values of the FC Cu could be a possible reason for the absence of superconductivity in these samples. The correlations between the composition, structural parameters and physical characteristics were found.

Keywords: CUPRATES, STRUCTURE, SUPERCONDUCTIVITY