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The Bond Valence Model and Point Defects in Langasite Family

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Crystals of langasite structure ($La_3Ga_5SiO_{14}$ - $La_3Ga(1)Ga_3(2)(GaSi)(3)O_{14}$) belong to the sp.gr. P321 and have four kinds of cation sites. The La, Ga(1), Ga(2) and (GaSi)(3) ions are located on a decahedral, octahedral, tetrahedral and trigonal-pyramidal sites, respectively.

In this work we demonstrate an analysis of the structure refinements of the langasite family compounds $La_3Ga_4(Ga_xSi_{2-x})O_{14}$, $La_3Ga_4[Ga(Si,Ge)]O_{14}$, $La_3Ga_{5.5}M_{0.5}O_{14}$ c M=Ta, Nb with the bond valence models. The calculation of bond valence (s_{ij}) for cation sites was made by the two methods:

- method of Brese and O'Keeffe: $s_{ij}=\exp[(R_{ij} - d_{ij})/b]$;
- method of Brown and Wu: $s_{ij}=(R_i/d_{ij})^{-N}$

The calculation of s_{ij} valus for cation and anion sites was fulfiled by Pyatenko method: $s_{ij} = k_i/d_{ij}^n$; $k_i=\upsilon_{kj}/\Sigma d_{ij}^{-n}$ (d_{ij} –cation-anion distance).

With these results, it is possible to confirm the occupancy of the (GaSi)(3) sites by some cations and their correlation, to suppose a presence of cation vacancies in La and Ga(1) sites, to prove a distribution of the Ta and Nb ions into two sites (Ga(1) and (GaSi)(3)) and one site (Ga(1)), respectively.

Keywords: langasite, point defects, bond valence method

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Synthesis, Structure and Photocatalysis in $LiBi_4Ta_3O_{14}$ and $LiBi_4Nb_3O_{14}$

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The application of photocatalytic materials in wastewater treatment, control of toxic air contaminants and remediation of hazardous wastes has been of interest. Several materials like TiO_2, pyrochlores and bismuth tantalates have been extensively studied. In search of novel structural types with enhanced photo-catalytic activities, a series of new compounds, $LiBi_4Ta_3O_{14}$ and $LiBi_4Nb_3O_{14}$ in the Li_2O-Bi_2O_3-$(Nb/Ta)_2O_5$ system have been isolated for the first time in the hitherto unknown lithium bismuth niobates and tantalates. Both the compounds crystallize in the monoclinic space group, C2/c with a = 13.115(2) Å, b = 7.583(1) Å, c = 12.226(2) Å, β = 101.477(3)°, V = 1182.6(5) Å^3 and Z = 4; a = 13.035(3) Å, b = 7.647(2) Å, c = 12.217(3) Å, β = 101.512(4)°, V = 1193.4(5) Å^3 and Z = 4 for $LiBi_4Ta_3O_{14}$ and $LiBi_4Nb_3O_{14}$ respectively. The structures were solved by direct methods and refined to R of 0.057 and 0.078. The crystal structure consists of layers of $[Bi_2O_2]^{2+}$ units separated by layers of LiO_4 tetrahedra and $(Nb/Ta)O_6$ octahedra hence depicting a new structural type.

The UV-Visible diffuse reflectance spectra suggest a band gap of 3.4eV and 3.2eV for $LiBi_4Ta_3O_{14}$ and $LiBi_4Nb_3O_{14}$ respectively. Photo-catalytic degradation of a wide range of dyes was studied.

Keywords: crystal structures, photocatalysis, dyes

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Peculiarities of the Electronic Structure and Dynamics in the Nanosystems

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From the experimental results with Electron Spin Resonance in combination with other methods, numerous special complexes of odd electrons in many different materials and biomedical nanosystems and the concerning unique effects have been revealed. The behaviour of these complexes shows some unusual characteristics very distinct from the ones in the normal crystalline systems. It is especially notable that these new effects stand in close connection with the fundamental properties of the materials such as the conformation, the conductivity, the biomedical activity.

Over a long period of time we have carefully persued these phenomena and come to the conclusion that they only can be adequately explained through a new consideration on the ground of the Structure and Dynamics of the Quasi-Free Electrons in the Short-Range Order of the nanosystems. On the basis of this elaborated model there is the possibility of a profound interpreting the molecular electronic mechanisms of the particular features and technological factors of the materials and biomedical nanosystems.

As illustration examples, the effect of strong crystal field, the effect of sudden change of the conductivity, the effect of radiation emission in some materials and biomedical systems, the molecular electronic mechanism of the toxicity of Dioxin, the superconducting nanomechanism in YBCO compounds, and other phenomena are briefly exposed and discussed.

Keywords: structure and dynamics in nanosystems, electron dynamics in nanostructures, electron dynamics in nanosystems

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High-temperature Structural Disorder in α-Quartz-Type Piezoelectric Materials

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Piezoelectric materials are used at high temperature in important technological applications such as microbalances, pressure sensors and field-test viscometers. At room temperature in the α-quartz group of materials, the piezoelectric coupling coefficient can be related to the structural distortion with respect to the β-quartz structure type. Piezoelectric properties of α-quartz resonators, however, begin to degrade well below the α-β phase transition temperature at 846 K. In order to identify new higher performance materials, it is essential to develop structure-property relationships *in situ* at high temperature.

Quartz and the promising homeotypic material $GaPO_4$ were studied at high temperature by total neutron scattering and by piezoelectric measurements. In contrast to the results of Rietveld refinements of the average structure, reverse Monte-Carlo refinements using total neutron scattering data indicate that structural disorder in quartz significantly increases well below the α-β transition. In the case of $GaPO_4$, an increase in disorder is observed beginning above 1023 K. Piezoelectric measurements indicate that the quality factor of $GaPO_4$ resonators begins to degrade at this temperature. This degradation can be correlated to the increase in structural disorder. Gallium phosphate is thus a promising material for applications at temperatures up to 1000 K.

Keywords: structure-property relationships, quartz, high-temperature structures

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Unusual Structural Properties of $(Na,Gd,Yb)WO_4$ and $(Na,La,Ce,Er)MoO_4$

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Single crystals of general formula $(Na^{+1},R^{3+})T^{6+}O_4$ (R^{3+}=Gd,La; T^{6+}=Mo и W), doped by Yb^{3+}, Ce^{3+}, Er^{3+} meet very high interest of different scientific groups as active media for solid-state lasers.

Crystals of $(Na_{0.5}Gd_{0.5-x}Yb_x)WO_4$ with x=0.0, 0.0025, 0.0075, 0.025, 0.10) and $(Na_{0.500}La_{0.495-x}Ce_xEr_{0.005})MoO_4$ with x=0.0, 0.10, 0.125, 0.15, 0.175, 0.20) belonging to sheelite family have been grown by Czochralski technique in a different atmosphere, treated by

a different conditions and studied by X-ray diffraction.

The $(Na_{0.5}La_{0.5})MoO_4$ with $|\Delta r_{(Na-La)}|=r_{Na}-r_R=0.02$Å (r-ionic radius) has the scheelite structure (sp. gr. $I4_1/a$), in contrast to the $(Na_{0.5}Gd_{0.5})WO_4$ ($|\Delta r_{(Na-Gd)}|=0.13$Å) and (Na,Gd,Yb)$WO_4$ ($r_{Na}>r_{Gd}>r_{Yb}$) with the pseudo-tetragonal superstructure unit cell with double parameters. The non-annealed (growth in Ar) and annealed by 1000ºC for 4 days in air crystals of $(Na_{0.500}La_{0.445}Ce_{0.05}Er_{0.005})MoO_4$ nominal composition have "enantiomorphic" structures. The annealed by 1000ºC for 24 h in air crystal of $(Na_{0.500}La_{0.295}Ce_{0.20}Er_{0.005})MoO_4$ has the scheelite structure. A statistical distribution of oxygen on two sites of structure of non-annealed (growth in $99\%N_2+1\%O_2$) and annealed by 700ºC for 100 h in air of these crystals was found.

Keywords: sheelite, structure, properties

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Lattice Parameters Measurements of $YBa_2Cu_3O_{7-\delta}$ Superconductors Prepared under Various Forming Pressures using X-ray Diffraction Technique

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The effect of pressure on the critical temperature T_c is studied for $YBa_2Cu_3O_{7-\delta}$ compounds prepared under various forming pressures. A systematic decrease in lattice parameters is observed with forming pressure. Resistivity measurements show an increase of the onset temperature T_{cO} with forming pressure. A value of $dT_{cO}/dP\approx(0.070\pm0.010)\times10^{-8}$ K/Pa is determined. A new mechanism based on the variation of the interlayer tunneling integral $t_\perp$ is used to analyse the experiment results.

Keywords: superconductors, lattice, parameters

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On a New Wave Type Generated in Deforming Metal Crystals

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Quasi-static deformation was studied on tensile fcc, bcc and hcp single crystals by holographic technique. It iahs been found that slow wave processes are generated in the deforming material. These involve concerted motion and temporal evolution of local flow nuclei whose nature is defined by micro-scale self-organization mechanisms.

The wave pattern type is determined for a given flow stage by work hardening law $\theta(\varepsilon)$, where $\theta=G^{-1}\cdot d\sigma/d\varepsilon$ is the work hardening coefficient; G, the shear modulus; σ, the plastic flow stress and ε, the deformation. The waves are characterized by wavelength $5\leq\lambda\leq10$mm propagation rate $10^{-5}\leq V\leq10^{-4}$m/s and frequency $10^{-3}\leq\omega\leq10^{-2}$Hz. The waves are found to exhibit the following regular features: wave rate $V=\Xi/\theta$, where $\Xi=const\approx10^{-7}$m/s; quadratic dispersion law $\omega(k)=1+k^2$ and a concurrent decreases in the entropy of material by wave generation $\Delta S<0$.

These can be likened to quasi-particles whose mass as calculated from the de Broglie equation for all the monocrystals tested $m=h/V\approx1.5$amu and dimensionless mass $\mu=m/A$ (A is the respective metal's atomic mass) are found to grow with the number of electrons n per metal unit cell as $\mu=\mu_0+\kappa n$.

Thus it is contended that by plastic flow slow waves would be generated spontaneously in a single metallic crystal, which is regarded as a complex thermodynamically open system. The nature of these wave processes and their role on plastic deformation are discussed.

Keywords: plasticity, wavelength, entropy

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Structure and Magnetic Properties of 3-substituted-5-(2-pyridyl) Pyrazole Metal(II) Complexes

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Five substituted pyridyl-pyrazole metal(II) complexes, [Fe(Hpp-*But*)$_3$(*X*)$_2$], *X*=ClO_4^- (***1***), BF_4^- (***2***), [Co(Hpp-*But*)$_3$(ClO$_4$)$_2$] (***3***), *cis*-[Fe(Hpp-ϕ)$_2$(NCS)$_2$] (***4***) and *trans*-[Fe(Hpp-ϕ)$_2$(NCS)$_2$]·(H$_2$O)$_2$ (***5***), were synthesized. Molecular and crystal structures of these complexes were investigated by single crystal structure analysis. The comparison in molecular structures between these complexes will be presented. The magnetic properties were studied by SQUID magnetometer.

Complex (***1***) and (***2***), with t-Butyl substituted group, are spin-crossover compounds. Complex (***1***) is a gradual but completed spin transition from RT to 200K. The Fe $L_{2,3}$-edge of iron(II) of (***1***) and (***2***) X-ray absorption spectroscopy are studied using synchrotron radiation. The apparent change due to HS-LS transition will be presented in coordination geometry around Fe and in Fe core electron excitation. However, compound (***4***) and (***5***), with substituted phenyl group, show no spin transition phenomenon within the temperature range studied. The relationship between structure and magnetic properties will be discussed.

Keywords: structure-magnetism relationships, spin crossover, magnetism

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X-ray Absorption Studies of Fe-btr Spin Crossover Complexes

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The aim of this work is to take the advantage of the X-ray absorption spectroscopy to get insight into the evolution of electronic configuration in HS and LS states of the specific absorption atoms at various temperatures and also in the LIESST state. Three Fe spin crossover complexes, (**1**) Fe(btr)$_2$(NCS)$_2$·H$_2$O[1], (**2**) Fe(btr)$_3$(ClO$_4$)$_2$[2] and a Co doped Fe_xCo_{1-x}(btr)$_2$(NCS)$_2$·H$_2$O[3] (**3**) were chosen to be studied. With temperature changing **1** shows an abrupt spin transition with a hysteresis of 25K ($T_{1/2}\downarrow$ = 119.8K and $T_{1/2}\uparrow$ = 145.1K) while **2** was found to behave as a two-step spin crossover complex.

K-edge absorption spectra of **1** and **3** were collected in both RT (HS) and 16K (LS) and also after irradiating by a laser light of 532 nm. The existence of the HS-2 after irradiation in both **1** and **3** is varified by Fe K-edge spectra. However, spin transition only occurs at Fe site not at Co site, though they should be situated on the same site.

Fe L-edge spectra of **2** illustrate a two-step spin transition; one is abrupt and the other one is gradual, which is consistent with the results reported earlier.

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Keywords: spin-crossover, X-ray absorption, Fe(II) complexes

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Change of Structure and Properties of System WC-Ti at Mechanical Activation

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Tungsten carbide is one of the most interesting representatives carbides transition of metals of maximum groups, which can have as cubic, and hexagonal crystallographic modification. In particular, cubic WC with structure as NaCl has rather wide area homogeneity on carbon and has high temperature melting, hardness and durability, and also propensity to formation double carbides with transitive 3d-metals. The data about peculiarities of the chemical bonding and changes in then electronic structure of the cubic WC at partial replacement of