

Keywords: rare earth and yttrium borates, vaterite structure, panel display phosphors (PDPs)

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Effects of Er³⁺ and Yb³⁺ doping on non linear properties of double lithium sulphates

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The crystalline network that characterizes the family of ferroic materials of the kind of $ALiSO_4$ ($A=Na, NH_4, K$) has a great flexibility, which facilitates the existence of phase transitions and non-linear properties. However, lately, the research has been basically directed to the ionic conductivity these networks present. The work we present here is a part of a research line on the effects of rare earths in non-linear matrixes due to their great technological interest. The study of the structural properties due to the doping of $LiNaSO_4$ with Yb^{+3} and Er^{+3} were performed by Palmero et al. (*J. Luminic.* 128, 2008). The doped compounds showed no important structural differences in relation to the pure ones. Apart from that and for the first time, they observed second harmonic generation (SHG) in all cases. In what refers to $LiNH_4 SO_4$, Gonzalez-Silgo et al. (2008. In Press), found two new alpha phase polymorph isotypes of the $Li(NH_4)_{1-2x} Yb_x SO_4$ doped compound, which present SHG. In this work, the Lithium-Potassium sulphate has been analysed using the same procedures and experimental techniques as in previous cases (RX, TG-DTA, DSC and SHG). The structural differences observed in the compounds doped with Yb^{+3} and Er^{+3} show some rotation with respect to the pure one. The data obtained from the three sulphates allow us to present a comparative study on the Yb^{+3} and Er^{+3} doping effect in relation to their non-linear optical properties in the context of the structure and the temperature behavior. The results are quantitatively discussed in two different ways: using the Bond-Valence Sum (BVS) model and the Abraham-Kurt-Jamieson criterion, which are compared with the model presented by Xue and Zhangs (*Phys. B* 262, 1999) for non-linear compounds.

Keywords: phase transition, Li-sulphates family, second harmonic generation

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$Ln_2(Ca,Mn)Ge_4O_{12}$ - New materials for photonics

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The new group of germanates $Ln_2M^{2+}Ge_4O_{12}$ ($Ln = Eu-Lu$; $M = Ca,$

Mn) was synthesized; their crystal structure and optical properties were studied. The crystal structure of these compounds can be described as two alternating layers: one formed by Ln and (Ca,Mn) atoms and another by tetracyclic polyatomic anions $[Ge_4O_{12}]^{8-}$ with boat conformation (sp.gr. $P4/nbm$). Between these layers octahedral and square antiprismatic cavities are formed. The Ln and (Ca,Mn) atoms are placed inside oxygen octahedrons with ratio 0.5/0.5. The square antiprisms are occupied only by rare earths cations. The decreasing atomic radius of the rare earth elements leads to a change of the isle structure motive to the 2D layered type. These compounds have an optical gap $E = 5eV$ and exhibit record Stokes shifts ($3500 - 4200 \text{ cm}^{-1}$) upon laser pumping at $\lambda=976 \text{ nm}$ in the stationary mode. The shift band consists of selected lines with a width of $5 - 8 \text{ cm}^{-1}$. High values of Stokes shifts are caused by inelastic interactions of excitation quanta and tetracyclic groups $[Ge_4O_{12}]$, which are harmonic oscillators. This type of vibration is almost absent in compounds with Yb and Lu with the 2D layout of tetracycles in the structure.

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Keywords: rare-earth luminescent materials, germanates, Raman spectroscopy

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Different ordered defect scheelite type in $RE_2(MoO_4)_3$ crystal structures

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The structural diversity of molybdates provides these materials with a wide variety of physical properties from an applied point of view. They are important host crystals for a variety of inorganic phosphors-converted light emitting diodes [1], tunable solid state laser material [2] and attractive χ^2 and χ^3 nonlinearities for second harmonic generation and stimulated Raman scattering [3]. The structural study was carried out on powered samples obtained by solid state reaction with the same heat-treatment. From Rietveld refinement, two types of isotypism were differently studied: 1) La-Sm molybdates show different ordered scheelite structure. Only the $La_2(MoO_4)_3$ structure is found in the ICSD data base and is described as an ordered defect scheelite structure. Partial ordering is found in Pr and Nd molybdate structures and $Sm_2(MoO_4)_3$ have a new ordered structure similar to $Eu_2(WO_4)_3$. Possible ordering schemes have been analyzed within the frame of a 2D Ising model [4], starting from the lattice completely randomised and using a Metropolis Monte-Carlo method. 2) Eu-Dy molybdates show the typical β - $Gd_2(MoO_4)_3$ ferroelectric structure (founded for Gd and Tb in ICSD). The structures are discussed, in a quantitative form, using the chemical bond theory of complex crystals and the modified bond charge model via two different routes: the Bond-Valence model sum and of the criterion of Abraham-Kurt-Jamieson.

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Keywords: rare earth molybdates, second harmonic generation (SHG), scheelite structure

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Application of statistical methods for the prediction of properties of organic solid forms

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We are investigating the application of appropriate statistical methods for the prediction of the formation and properties of organic solid forms, taking advantage of the possibility to determine structures and properties of family sets of organic solid forms using High Throughput Chemical Crystallography. Statistical models are being built to relate quantitative descriptors of molecular or crystalline structure to the classification of compounds, and to predict measured properties of the compounds, such as melting point and enthalpy of fusion. In many of these studies, a large number of quantitative variables are available as potential predictors of a response. The sizes of available datasets and feasible experiments (small to medium), often result in there being more potential descriptors than data points. We are therefore exploring the selection of statistically relevant subsets of the possible descriptors. A further complication is the need to consider nonlinearities in the statistical models and interactions between the variables. A variety of data forms are being considered, including binary data for the classification problem, categorical data when considering the occurrence of polymorphs and continuous data for measured properties. Appropriate statistical methods are being developed, where necessary, and applied to each situation, based on methods such as generalised linear and additive models, recursive partitioning and classification trees, and ensemble models. The performance of different methods are being critically assessed and compared. The poster will present results obtained so far.

Keywords: statistical methods, crystal structures, property prediction

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High hardness and incompressibility in transition metal borides

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Transition metal borides have recently gained high interest as potential superhard materials. Despite the high costs for the transition metals, their synthesis is comparably facile and can be done at ambient pressure conditions, what favours them for example against c-BN or advanced nanocomposite materials for a potential use in industrial applications. In a systematic study, we synthesized borides of Ru, W, Re, and Os. The crystal structures of these materials are characterized by a different packing of transition metal and flat and/or puckered boron layers. The mechanical properties were determined by microindentation as well as compressibility measurements using diamond-anvil cells and synchrotron radiation. The observed

properties of the materials can be understood based on their crystal structures and the chemical bonding. The analysis of the chemical bonding of these compounds by means of the electron localization function (ELF) revealed a high degree of covalent boron-boron bonding as a necessity for a high hardness. On the other hand, as it is well known, a high electron concentration yields to an incompressible material. Therefore, OsB was found to be the most incompressible, WB₄ the hardest of the investigated materials. A good compromise between incompressibility and hardness was found for WB₂, (W,Os)B₂ and the isoelectronic ReB₂. We thank the staff of the MS beamline at Swiss Light Source (SLS at PSI, Villigen, Switzerland) for experimental assistance

Keywords: borides, bulk modulus, microhardness

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Structure and magnetic study of solvated and non-solvated spin crossover complex [Fe(SalEen)₂]ClO₄

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The water solvated [Fe^{III}(SalEen)₂]ClO₄·0.5H₂O (**1**) and non-solvated [Fe^{III}(SalEen)₂]ClO₄ (**2**) complexes were synthesized and structure characterized (SalEen = N-(2-ethylamino)ethyl-salicylaldehyde). Complex **1** crystallizes in the polar orthorhombic space group *Fdd2* with cell parameters $a = 18.4301(7)$, $b = 55.7300(20)$, $c = 9.9021(3)$ Å, $V = 10171.1(6)$ Å³, $Z = 16$, while complex **2** crystallizes in the monoclinic space group *P2₁/c* with $a = 9.9440(2)$, $b = 21.1875(5)$, $c = 12.3637(3)$ Å, $\beta = 104.311(1)^\circ$, $V = 2524.1(1)$ Å³, and $Z = 4$. The water molecule induces a very different molecular packing situation which causes distinct magnetic property between the solvated and non-solvated complexes. The thermal dependent magnetic measurement shows gradual spin transition property for both complexes, both are in the high spin (HS) state $S = 5/2$ at 350 K and convert to the full low spin (LS) state $S = 1/2$ below 30 K for **1** ($T_{1/2} = 155$ K) and 120 K for **2** ($T_{1/2} = 230$ K). A two-step spin transition is interested found in complex **1**, which represents the first Fe(III) system with such behavior. Crystal structures of the LS state at 25 K for **1** and at 100 K for **2** are collected for comparison to the HS state structures at 300 K. The bond lengths associated with the FeN₄O₂ octahedron in the HS and LS states are consisted with the magnetic result. The Fe-N_{avg} and Fe-O_{avg} differences are 0.148 and 0.034 Å shorter for **1** and 0.132 and 0.027 Å shorter for **2** in the LS state, respectively. Also the octahedral distortion parameters Σ and Θ , defined as the sum of the absolute values of the deviation from 90° of the 12 cis angles and deviations from 60° of the 24 possible angles in the coordination sphere, show the more closely to normal octahedral environment in the LS state as expected.

Keywords: structural and magnetic phase transitions, magnetic behaviour, single-crystal characterization

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Structural-microstructural & magnetic properties relationships of In_{1.0}Fe_{0.1}Te_{0.9}, In_{1.0}Co_{0.1}Te_{0.9}

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