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Keywords: photoluminescence, gallium oxalato-phosphate, organic-inorganic hybrid material

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New 1D, 2D and 3D azido Mn, Cd and Zn complexes with magnetic and non-linear optical properties

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Supramolecular chemistry is concerned with weak interactions that occur between molecules, i.e. all non-covalent bonds, as well as weak coordination bonds. Such interactions are important in biological, magnetic and optical systems. Here we describe coordination compounds used as building blocks in crystal engineering. We present a number of supramolecular 1-D, 2-D and 3-D complexes of Mn^{II}, Cd^{II} and Zn^{II} with the azido bridge as a networking agent. The versatility of the azide ligand affords chains with Mn^{II} in which ferrimagnetic behavior is clearly observed for 1-D and 2-D Mn^{II} systems with quinoline derivatives [Mn(H₂O)(μ-N₃)(N₃(quinaz)₂)_n and [Mn(μ-N₃)₂(quinaz)₂]_n (quinaz = quinazoline) and [Mn(μ-N₃)₂(pyzamid)₂]_n and [Mn₂(3-ampy)₄(μ-N₃)₂(N₃)₂(H₂O)₂]_n (pyzamid = pyrazineamide and 3-ampy = 3-aminopyridine). The field of non-linear optics (NLO) is of considerable interest for many commercial applications. In particular, second-order harmonics generation, i.e. frequency doubling, which can be used in the conversion of red laser into blue laser light, is a desirable property. This requires a lack of inverse centre, an easy task in crystal engineering of coordination polymers with chiral components. We report the synthesis, spectral and structural characterization of some Cd^{II} and Zn^{II} complexes. The Kerr effect was studied as a property of the NLO materials for complexes [Cd₃(nic)₄(N₃)₂(H₂O)₂]_n, [Zn(nic)(N₃)]_n (nic = nicotinate anion), [Cd(2,5-dmpyz)(N₃)₂]_n, (dmpyz = dimethylpyrazine) and [Zn(bipy)(N₃)₂]_n (bipy = 2,2'-bipyridine).

Keywords: supramolecular structures, metal-organic compounds, structure-function relationships in solids

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Motion of inclusion gas molecules in clathrate hydrate observed by neutron powder diffraction

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Methane hydrate has attracted great interest as an energy resource after the discovery in the deep seabed as huge reservoirs of methane gas. Moreover, carbon dioxide hydrate is paid much attention as a storage medium of carbon dioxide gas to prevent the global warming. These clathrate hydrates are inclusion compounds in which the hydrophobic guest molecules exist in a host ice-framework called 'cage'. Their structural stabilities are deeply related with the physical properties of inclusion gases. In this study, we carried out neutron powder diffraction measurements of carbon dioxide and Xe deuterohydrates using the HRPD at JRR-3, JAEA. The diffraction data were analyzed by the combination of the Rietveld and the maximum entropy method (MEM) to clarify the motion of inclusion gases. The motions of carbon dioxide and Xe molecules in the small cages show the different manner from those in the large cages. These motions have small temperature dependences, in contrast to the methane hydrate case where the motion of methane molecules in the large cage shows large temperature dependence. Details on the motions of gas molecules in the hydrates are discussed.

Keywords: clathrate hydrate, neutron powder diffraction, MEM

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Possible non-centrosymmetric structure of vaterite type yttrium orthoborate

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Yttrium and Lanthanide Orthoborates are promising candidates to be used in new-generation flat-panel display phosphors technologies. Despite extensive research on the Eu³⁺ luminescence, in these compounds, fundamental questions remain unanswered regarding the relation between the vaterite type structure and the resulting Eu³⁺ spectral features. High-resolution luminescence spectra do not permit to unambiguously distinguish between the alternatives of having either two or three cation sites in the structures, which are compatible with the crystal structures solved by single-crystal X-ray and neutron powder diffraction, respectively. Three samples: YBO₃, Y_{0.85}Eu_{0.15}BO₃ and Y_{0.85}Yb_{0.15}BO₃ were prepared by solid-state reaction. We have undertaken an investigation, combining optical spectroscopy, second harmonic generation, X-ray powder diffraction and first-principles calculations, to correlate the optical features with the crystalline structure. Some remarkable results have been achieved: 1) all the samples show similar SHG intensities than the KDP and these increases with the doping concentration; 2) from Rietveld refinement and first-principles calculations we can distinguish between the hexagonal, orthorhombic and monoclinic symmetry. Moreover, doped samples are better refined in the acentric C₂ space group, thus, we can correlate the number of sites of Yttrium and point symmetry with the results obtained from Yb³⁺ and Eu³⁺ optical spectra. Complementary first-principles total-energy calculations also are shedding light in the structural analysis of the systems [1].

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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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