Motion of inclusion gas molecules in clathrate hydrate observed by neutron powder diffraction
Naoko Iga1, Tomitsugu Taguchi1, Hiroshi Fukazawa1, Hiroki Yamauchi1, Yoshinobu Ishii1, Wataru Utsumi1
1Japan Atomic Energy Agency, Quantum Beam Science Directorate, 2-4 Shirane, Tokai-mura, Ibaraki-ken, 319-1195, Japan, 2Radiation Application Development Association, Tokai-mura, Ibaraki-ken 319-1106, Japan, E-mail: igawa.naoki@jaea.go.jp

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

Possible non-centrosymmetric structure of vaterite type yttrium orthoborate
Victor M. Sanchez Fajardo, Antonio D Lozano-Gorrin, Patricia Haro, Fernando Rivera-Lopez, Silvana Radescu, Andres Mujica, Inocencio R. Martin, Manuel E. Torres, Cristina Gonzalez-Silgo
Facultad de Fisica - Universidad de la Laguna, Fisica Basica, Astrofisico Francisco Sanchez, La Laguna, Santa Cruz de Tenerife, 38204, Spain, E-mail: vimasafa@ull.es

Yttrium and Lanthanide Orthoborates are promising candidates to be used in new-generation flat-panel display phosphors technologies. Despite extensive research on the Eu13+ luminescence, in these compounds, fundamental questions remain unanswered regarding the relation between the vaterite type structure and the resulting Eu13+ 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: YBOs1, Ys8.65Eu1.35BO3 and Y0.88Yb0.11BO3 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 Yb13+ and Eu13+ optical spectra. Complementary first-principles total-energy calculations also are shedding light in the structural analysis of the systems [1].

Poster Sessions

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Effects of Er\(^{3+}\) and Yb\(^{3+}\) doping on non-linear properties of double lithium sulphates

Manuel E Torres, Cristina Gonzalez-Silgo, Nanci S.P. Sabalisck, Fernando Rivera-Lopez, Patricia Haro-Gonzalez, Antonio D. Lozano-Gorrin, Victor M. Sanchez-Fajardo, Ulises R Rodriguez-Mendoza

Fac. de Fisica - Universidad de la Laguna, Fisica Basica, Av. Astrofisico Francisco Sanchez S/N, La Laguna, Sta. Cruz de Tenerife, 38204, Spain, E-mail:metorres@ull.es

The crystalline network that characterizes the family of ferroelectric 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 polyimorph isotypes of the Li(NH\(_4\))\(_{1-2}\)X YbXSO\(_4\) 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 sulphaes 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-Jamiensson 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)GeO\(_4\) - New materials for photonics

Ivan I. Leonidov\(^{1}\), Vladimir G Zubkov\(^{1}\), Nadezda V Tarakina\(^{1}\), Alexander P Tutyunnik\(^{1}\), Ludmila L Surat\(^{1}\), Inna V Baklanova\(^{1}\), Lina A Perelyaeva\(^{1}\), Olga V Koryakova\(^{2}\), Joke Hadermann\(^{2}\), Gustaf Van Tendeloo\(^{2}\)

\(^{1}\)Institute of Solid State Chemistry, the Ural Branch of the Russian Academy of Sciences, 91, Pervomayskaya, Yekaterinburg, Sverdlovsk, 620219, Russia. \(^{2}\)Institute of Organic Synthesis, the Ural Branch of the Russian Academy of Sciences, 22, S.Kovalevskaya, Yekaterinburg, 620219, Russia. \(^{1}\)EMAT, University of Antwerp, Groenenborgerlaan 171, Antwerp, Belgium, E-mail:IvanLeonidov@ihim.uran.ru

The new group of germanates Ln\(_{2}\)(Ca,Mn)GeO\(_4\) (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\(_6\)O\(_{18}\)]\(^+\) with boat conformation (sp.gr. P4/nmm). Between these layers octahedral and square antiprismic 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 iso structure motif to the 2D layered type. These compounds have an optical gap E = 5eV and exhibit record Stokes shifts (3500 - 4200 cm\(^{-1}\)) upon laser pumping at \(\lambda=976\) nm in the stationary mode. The shift band consists of selected lines with a width of 5 – 8 cm\(^{-1}\). High values of Stokes shifts are caused by inelastic interactions of excitation quanta and tetracyclic groups [Ge\(_6\)O\(_{18}\)], 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

Antonio D. Lozano-Gorrin, Victor M. Sanchez-Fajardo, Manuel E. Torres, Cristina Gonzalez-Silgo, Silvana Radescu, Andres Mujica, Nanci S.P. Sabalisck, Ivan Da Silva, Victor Lavin
Fac. de Fisica - Universidad de La Laguna, Fisica Fundamental y Experimental, Av. Astrofisico Francisco Sanchez, S/N, La Laguna, Sta Cruz de Tenerife, 38204, Spain, E-mail:adlozano@ull.es

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 \(\chi^2\) and \(\chi^3\) 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(MoO\(_4\))\(_3\) have a new ordered structure similar to Eu(WO\(_4\))\(_2\). 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 \(\beta\)-Gd(3MoO\(_4\))\(_2\) 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.