

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

P08.14.162

Acta Cryst. (2008). A64, C468

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

Manuel E Torres, Cristina Gonzalez-Silgo, Nanci S.P. Sabalisk, 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 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

P08.14.163

Acta Cryst. (2008). A64, C468

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

Ivan I. Leonidov¹, Vladimir G Zubkov¹, Nadezda V Tarakina¹, Alexander P Tyutyunnik¹, Ludmila L Surat¹, Inna V Baklanova¹, Lina A Perelyaeva¹, Olga V Koryakova², Joke Hadermann³, Gustaaf Van Tendeloo³

¹Institute of Solid State Chemistry, the Ural Branch of the Russian Academy of Sciences, 91, Pervomayskaya, Yekaterinburg, Sverdlovsk, 620219, Russia, ²Institute of Organic Synthesis, the Ural Branch of the Russian Academy of Sciences, 22, S.Kovalevskaya, Yekaterinburg, 620219, Russia, ³EMAT, University of Antwerp, Groenenborgerlaan 171, Antwerp, Belgium, E-mail: IvanLeonidov@ihim.uran.ru

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.

This work was supported by the RFBR (grant 07-03-00143), by the Councils for Grants of the President of Russia for Support of Young Scientists (grant MK-84.2007.3) and for Support of Leading Scientific Schools (grant NSh-1170.2008.3).

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

P08.14.164

Acta Cryst. (2008). A64, C468-469

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. Sabalisk, 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 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.

[1] G. Yi, B. Sun, F. Yang, D. Chen, Y. Zhou, J. Cheng. *Chem. Mater.* 2002, 14, 2910-2914. [2] A. Méndez-Blas, M. Rico, V. Volkov, C. Zaldo, and C. Cascales. *Phys Rev BPhys. Rev. B* 75, 174208 (2007). [3] M. J. Weber. *CRC Handbook of Laser Wavelength* (CRC Press Boca Raton, 2000). [4] Radescu, S., Etxebarria, I., Perezmató, J.M. J.