

**FA2-MS07-O1****Rare Earth Calcium Oxoborate Family,  $\text{Ca}_4\text{REO}(\text{BO}_3)_3$  (RE = Gd, Y, Sc, Lu, Nd, Yb): a Real Challenge to Design Nonlinear Crystals for Frequency Conversion in Visible and UV Range.**

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More than ten years ago the nonlinear optical properties of calcium Rare Earth oxoborate  $\text{Ca}_4\text{REO}(\text{BO}_3)_3$  (RE = Gd, Y, Nd) was demonstrated [1-2]. Large size crystals were grown for the first time by Czochralski pulling process. GdCOB ( $\text{Ca}_4\text{GdO}(\text{BO}_3)_3$ ) was the first member of this oxoborate crystals family to be elaborate in large dimensions (50 mm of diameter and 100 mm of length). The first works done on these materials were devoted to the demonstration of the quadratic non-linear optical properties of this new borate family [1-2]. GdCOB was shown to be an efficient nonlinear optical crystal. This crystal has been very well characterized regarding all the linear and nonlinear properties. The effective NLO coefficient is about 1pm/V. Its damage threshold is up to 1Gw/cm<sup>2</sup> at 1064 nm (6 ns pulses). The SHG conversion efficiency of a Q switch Nd:YAG laser is over 50%. In addition the thermal acceptance of GdCOB was found to be more than 325°C. cm at 1064 nm in the SHG configuration, which is relevant to be the best value for an NLO material.

Since the first evidence of large size crystal tremendous works have been done by different groups of the scientific community to develop other member of the oxoborate family [4-6]. Very recently large aperture  $\text{Ca}_4\text{YO}(\text{BO}_3)_3$  (YCOB) crystals with 75 mm diameter were grown for high-average power frequency conversion on the mercury laser system. High-average power frequency conversion of the mercury laser using YCOB has been demonstrated, and experimental validation of YCOB material yield 50% conversion at 10 Hz has been achieved.

Another example is that, in  $\text{Gd}_4\text{Ca}_4\text{O}(\text{BO}_3)_3$  (GdCOB) crystal, the  $\text{Gd}^{3+}$  ions can be partially substituted by  $\text{Sc}^{3+}$  or  $\text{Lu}^{3+}$ , in order to tune the chemical composition of the crystal. It is possible to achieve non-critically phase matching (NCPM) in the range of 780-963 nm and 920-963 nm which are very attractive wavelength for practical applications in the visible.

It is also possible to tune this oxoborate composition by substitution of  $\text{RE}^{3+}$  and  $\text{O}^{2-}$  by  $\text{Ca}^{2+}$  and  $\text{F}^-$ . This type of substitution lead to obtained the calcium fluoroborate  $\text{Ca}_3(\text{BO}_3)\text{F}$  (CBF) presenting a UV cut off lower than 190 nm [3]. CBF shows an incongruent melting behaviour. Flux growth method, allows obtaining CBF crystals with very good optical quality chemically stable and not hygroscopic.

This calcium rare-earth oxoborate crystal family shows optical properties, which uniquely make it multifunctional materials. The benefit of congruent melting behavior, allowing large and good optical quality crystals, suitable

sites for luminescent ions and good non-linear properties make this oxoborate family very attractive for various optical applications. The crystal growth of this calcium rare-earth oxoborate family will be discuss in relation with the possibility of achieving visible laser by frequency conversion for practical applications from UV to visible range.

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**Keywords: nonlinear optical materials; crystal growth; nonlinear optical properties**

**FA2-MS07-O2****New Nonlinear-laser Potential of Diamond, a-Quartz, Fluorite, and Calcite.** Alexander A. Kaminskii. *Institute of Crystallography, Russian Academy of Sciences, Moscow*.

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Crystals that are  $\chi(3)$ - or  $\chi(2)+\chi(3)$ -active offer a wide range of possibilities for the generation of new coherent wavelengths of light. Frequency conversion processes such as stimulated Raman scattering, second and third harmonic generation, or parametric sum frequency mixing can be effectively in the same nonlinear-laser crystals. In this report will be present short review of observed new manifestations of these effects in diamond, a-quartz, fluorite, calcite, and other crystals.

**Keywords: nonlinear laser crystals; second harmonic generation; stimulated raman scattering (SRS)**

**FA2-MS07-O3****Salts of Guanidine Derivatives – New Materials for Non-linear Optics.** Michaela Fridrichová<sup>a</sup>, Ivan Němec<sup>a</sup>, Ivana Císařová<sup>a</sup>, Petr Němec<sup>b</sup>. <sup>a</sup>*Department of Inorganic Chemistry, Charles University in Prague, Faculty of Science, Albertov 2030, 128 43 Prague 2, Czech Republic*. <sup>b</sup>*Department of Chemical Physics and Optics, Charles University in Prague, Faculty of Mathematics and Physics, Ke Karlovu 3, 121 16 Prague 2, Czech Republic*.

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Search for new materials exhibiting non-linear optical (NLO) properties belongs to important goals of materials research. NLO materials serve as optical elements in devices for signal and data processing and for optical communication. They have a wide range of use from electronics and microscopy to human medicine. For being capable of non-linear optical properties, the molecule must be non-centrosymmetric, i.e. its first order molecular hyperpolarizability  $\beta$  must be of non-zero value. Unfortunately, many of the acentric organic

compounds promising for NLO undergo dimerisation and crystallize in a centrosymmetric assembly. To avoid this, salts of organic cations were prepared, while the anionic network could prevent the dimerisation. The compounds reported in this contribution belong to the promising group of salts of polarizable organic cations with delocalized  $\pi$  – electrons, exhibiting so-called Y-aromaticity. Their cationic part is a guanidine derivative, connected with the anionic part by hydrogen bonds. The anionic part can be either inorganic (leading usually to chemical stability and resistivity) or organic (if chiral, providing acentric structure assembly). Properties of the final salt can be finely tuned by methods of crystal engineering – e.g. substitutions on the cation molecule, use of similar but slightly different anions etc. The structure of the material is determined. The measurement of second harmonic generation efficiency of the powdered sample including phase matching tests crowns the study of the material and the results are compared to the commercially available NLO materials as KDP (kalium diphosphate) or urea. The systematic “scanning“ of groups of novel compounds with focus on the relation between their structure and optical properties is an efficient method of this branch of materials research.

**Keywords:** non-linear optics; crystal engineering; guanidine derivatives

#### FA2-MS07-O4

**Surface and Interface Study of Vanadium Oxide Nano Films.** Ramis Mustafa Oksuzoglu. *Department of Materials Sciences and Engineering, Anadolu University, 26555 Eskisehir, Turkey.*

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Thin films of complex metal oxide systems (CMOS) as Vanadium Oxide [1-3] have gained great interest in recent years due to their potential applications in various optoelectronic devices. Among them including V<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, V<sub>6</sub>O<sub>13</sub>, VO<sub>2</sub> exhibit phase transition from semiconductor phase to metal phase (Semiconductor-metal transition, SMT) [4] in the temperature range from 50 °C to 70 °C [5] and this change has gained strong interest in recent years due to accompanying effects as the high temperature coefficient (TCR) used in uncooled microbalometers [1, 3] and charge intercalation used in electro-chromics [6-8]. There are only few investigations on the thickness dependence [9-12] and they indicated that the thin VO<sub>x</sub> films (<100nm) deposited at low process temperatures (200 °C) indicate amorphous structure, and films deposited at high temperatures (500 °C) indicate a polycrystalline structure with promising VO<sub>2</sub> phase. At low process temperatures (300 °C), VO<sub>2</sub> films possess with good TCR and ROS properties can only be obtained at high thicknesses of 1000 nm. We have produced VO<sub>x</sub> thin films of 37nm using DC-Reactive Magnetron Sputtering at room temperature and measured a TCR value of 2.3% C-1 with a high ROS of 1490 kΩ. In the present study, the thickness dependent structural evolution of VO<sub>x</sub> films in thickness range between 20nm - 50nm have been discussed in correlation to TCR and ROS values using X-Ray Reflectivity and Atomic Force Microscopy.

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**Keywords:** X-ray reflectivity; atomic force microscopy; resistivity; metal oxide thin films; sensors