## FA2-MS07-P01

Switching from Negative to Positive Nonlinear Absorption in Sn Doped GaSe Crystal. <u>Ayhan</u> <u>Elmali</u><sup>a</sup>, Mustafa Yüksek<sup>a</sup>, Mevlüt Karabulut<sup>b</sup>, G. M. Mamedov<sup>b</sup>. <sup>a</sup>Department of Engineering Physics, Faculty of Engineering, Ankara University, 06100 Beşevler, Ankara, Turkey. <sup>b</sup>Department of Physics, Kafkas University, 36100 Kars, Turkey. E-mail: elmali@eng.ankara.edu.tr

GaSe is one of the promising nonlinear crystals for middle-infrared frequency conversion, since GaSe layered crystals have low absorption coefficients in broad optical wavelengths, from near to far-infrared region (0.65-18  $\mu$ m), and they are transparent through this region [5-6]. The structure of GaSe is characterized by a strong anisotropy in the chemical bonding. Each covalently bonded layer consists of four monoatomic sheets in the order Se - Ga -Ga – Se [1,7]. The single layer is hexagonal and the c-axis is perpendicular to the layer plane. The layers are bounded together by weak van der Waals forces. In spite of its many attractive features, GaSe crystal is difficult to be cut and polished along some arbitrarily chosen directions while further improvement in the optical and mechanical properties of GaSe crystal is highly desirable for laser applications. The doping of GaSe crystal seems to be the optimal method to improve its optical and other physical properties. GaSe crystals can be both p- or n-type semiconductors, depending on growth conditions and dopant atoms.

In this study, Sn doped GaSe crystals were grown using conventional Bridgman method from a stoichiometric mixture of high purity Ga (99.9999%) and Se (99.999%) in evacuated quartz ampoules (10<sup>-4</sup> Torr) whose inner walls were coated with graphite [24]. Sn doping was done by adding the 0.5 at% Sn to initial batch composition. The UV-Vis absorption spectra of the Sn doped GaSe crystal was recorded using a scanning spectrophotometer (Shimadzu UV-1800), and the bandgap of crystal determined as  $\sim 2$ eV, with help of spectra. The nonlinear optical absorption of 0.5 at% Sn doped GaSe crystal was examined by openaperture Z-scan method. Z-scan experiments were carried out with nano- and picosecond laser sources. When Z-scan experiments of GaSe crystal which have been carried out at 1064 nm wavelength exhibited two photon absorption (TPA) [3,8,9], for the first time, we observed a switching from negative nonlinear absorption (saturable absorption, SA) to positive nonlinear absorption (two photon absorption, TPA) in Sn doped GaSe crystal by increasing laser intensity.

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Keywords: nonlinear absorption; z-scan; Sn doped GaSe crystal

## FA2-MS07-P02

Low Temperature Crystal Structure of  $\text{Li}_2\text{B}_4\text{O}_7$ . <u>Anatoliy Senyshyn</u><sup>a</sup>, Yaroslav Burak<sup>b</sup>, Volodymyr Adamiv<sup>b</sup>, Hartmut Fuess<sup>a</sup>. *aInstitute of Material Science, Darmstadt University of Technology, Darmstadt, Germany. bInstitute of Physical Optics, Lviv, Ukraine.* 

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The crystal structure of lithium tetraborate  $Li_2B_4O_7$  is known for a long time since the publication of Krogh-Moe [1]. Its structure at room temperature is tetragonal with the space group  $I4_1cd$  (point group 4mm) and with the polar axis along the crystallographic *c*-direction. The crystal structure is formed by a boron-oxygen network throughout the crystal with metallic atoms in the interstices. The anion  $B_4O_7^{2^-}$  - the basic subunit of this net consists of four boron atoms, where two of them are tetrahedrally and two other are triangularly linked to oxygens. To our knowledge  $Li_2B_4O_7$  type of structure as well as the existence of an isolated  $B_4O_7$  unit are unique and they do not occur in nature for any materials other than  $Li_2B_4O_7$ .

Recently, lithium tetraborate has attracted considerable interest in nonlinear optics especially as an element of surface acoustic wave (SAW) devices, which stimulated deeper studies of its properties, especially at non-ambient conditions.

In the literature there is plenty of controversial data on  $Li_2B_4O_7$  reporting either no anomalies or anomalous behaviour in the temperature range between 80 and 250 K, e.g. thermal scintillations have been observed in  $Li_2B_4O_7$  when not excited by hard quanta [2], incommensurate structure modulation [3], anomalies in thermal dependencies of lattice parameters and bond lengths [4, 5], large number of phase transitions [6, 7], anomalies in sound velocities and Raman spectra [8]. The existing discrepancies between the experimental results of different authors lead us to perform systematic studies of lithium tetraborate crystals.

Due to relatively poor sensitivity of X-ray diffraction to Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> constituents structural studies were performed using elastic neutron scattering. For this purpose the  $Li_{2}^{11}B_{4}O_{7}$  crystal (99.6% <sup>11</sup>B) has been grown using Czochralski technique. Powder diffraction examinations unambiguously indicated stability of Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> structure type in the temperature range 3-300 K. However, obvious anomalies in thermal dependencies of lattice parameters in c-direction (fully consisting with performed dilatometric studies), bond lengths and displacement parameters occurred. Crystal structure considerations yield the presence of discontinuous Li chains in c-direction of Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> structure, whilst extended bond length analysis revealed relatively high stability of  $B_4 O_7$  complex anion, thus enabling treatment of Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> as a diatomic solid consisting of  $Li^{1+}$  and  $B_4O_7^{2-}$ , as well as correlated motion of Li and B<sub>4</sub>O<sub>7</sub>. In the current contribution we report on complex studies of lithium tetraborate doped with <sup>11</sup>B in the broad temperature range using neutron powder/single

25<sup>th</sup> European Crystallographic Meeting, ECM 25, İstanbul, 2009 Acta Cryst. (2009). A**65**, s 213