Precipitation and dissolution in melt-grown GaSe crystals doped with sulfur or rare-earth metals

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The layered semiconductors, GaSe crystals are grown from melt for laser optics. We have developed a technique, which provides structurally perfect, stoichiometric GaSe crystals [1]. This material gets more and more interest as a crystal for nonlinear optics, since it can work as a frequency converter in IR and THz ranges. In this connection it is important to use isovalent and non-isovalent doping elements to enhance efficiency of second harmonic generation (SHG). Therefore, an idea was considered to use isomorphic small sulfur atoms for doping. Light doping with S from 0.01 to 0.5 at.% improved GaSe optical properties [2]. We have studied the range of sulfur doping from 0 to 100 at%. All materials were first synthesized and then crystals were grown from melt in argon atmosphere. We used XRD to analyze phase composition of the grown crystals. The diffraction patterns show presence of just one phase in all cases. Shifts of peaks point to the fact that all sulfur dissolves in GaSe. The calculated unit cell parameters shows linear character of concentration dependence typical of regular solutions. Measured optical and photoluminescence spectra have shown increase in band gap width and shift of fundamental absorption to blue edge as well as increase in PL intensity with increase in sulfur content.

A new approach to enhancement of nonlinearity of GaSe crystals is doping them with Er. It occurs that doping with erbium can improve optical properties, but erbium dissolves weakly and forms precipitates, which brings to light scattering [3]. Most precipitates are high-melting ErSe particles. We made an effort to avoid formation of these particles and to increase solubility of Er in GaSe moving to metastable state via development of synthesis and cooling conditions, which proved to be sensible, since we reached up to 0.3at%Er solubility for the $Ga_{0.99}Er_{0.01}Se$ initial composition, which is by an order of magnitude higher than in the melt-grown Er-doped GaSe reported in [3]. Temperature gradient in the furnace has a considerable effect on phase state of synthesized crystals. The crystal quenched from hotter zone contains just solid solution, while the crystal from cooler zone contains solid solution with the same unit cell parameters and a small amount of Er_2Se_3 phase, which was confirmed both by XRD and EPMA measurements. There is a SEM image in secondary electrons showing these particles in Fig. 1b. To continue our study of precipitation and solution of doping elements, we are going to grow GaSe:Er from melt using the synthesized material in order to homogenize Er distribution and improve crystallographic perfection of the synthesized polycrystals, which contain a lot of stacking faults due to disordered growth of domains in (0001)plane.

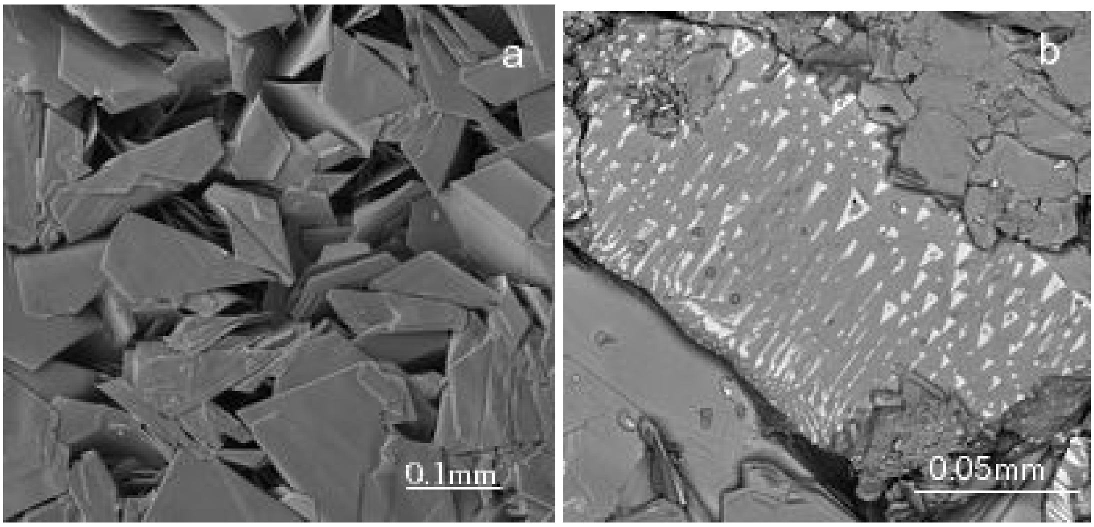

Figure. 1. SEM images of GaSe:Er synthesized crystals: (a) hot zone; (b) cold zone

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