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## STRUCTURAL CHARACTERIZATION OF III-VI SEMICONDUCTORS

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**Abstract:** The structural analysis of some III-VI compounds has been performed by Convergent Beam Electron Diffraction, in order to correlate the polytypism of such compounds both with methods and conditions of growth.

### 1. Experimental and results

GaS, GaSe and InSe crystals are very interesting materials both for their layered structure and for the anisotropy of their properties, which make them good candidates to be utilized in technology. In these compounds each layer contains two metal and two anion sublayers in the stacking sequence anion-metal-metal-anion. The bonding between two adjacent layers is of the Van der Waals type, while within the layer the bonding is mainly covalent[1]. The weak bonds between the layers give rise to different stacking sequences[1].

1) Two hexagonal polytypes obtained by the spatial repetition of a pair of fourfold layers: in the  $\beta$  polytype the second layer is  $60^\circ$  rotated with respect to the first one (space group  $P6_3/mmc$ ); in the  $\epsilon$  polytype the second layer is  $[10.0]$  translated with respect to the first one (space group  $P\bar{6}m2$ ).

2) The  $\gamma$ -3R rhombohedral polytype, made up by the spatial repetition of three layers (space group  $R3m$ ), obtained by adding a  $[10.0]$  translated layer to the  $\epsilon$  polytype.

In addition, less common structural modifications have been observed: the  $\delta$  hexagonal polytype with c-axis double of the  $\epsilon$  structure (space group  $P6_3mc$ ), and the 9R, 12R and 15R rhombohedral modifications.

The crystals have been grown in our laboratory by using two different methods of growth[1]. Large InSe, GaS and GaSe crystalline ingots have been obtained from the melt by using the Bridgman-Stockbarger method, according to procedures described elsewhere. In addition, GaSe single crystals have been obtained by adding different quantities of sublimed Iodine (0.5, 1.0, 2.0, 2.5, 3.5 and 4 mg/cm<sup>3</sup> ampoule volume) to the starting charge. Single crystal platelets of GaS and GaSe have been grown from the vapour by the chemical transport by using a quantity of sublimed Iodine corresponding to 2 mg/cm<sup>3</sup> ampoule volume in GaS growths, while the Iodine concentration has been varied between 0 and 3 mg/cm<sup>3</sup> in GaSe growth runs.

The structure analysis has been performed by convergent beam electron diffraction by using a Philips EM 400T microscope.

The GaS structure has been found to be the  $\beta$  phase, independently on the growth method.

The analysis of melt grown InSe shows the material is made up of four different structural modifications: the  $\epsilon$  and the  $\delta$  hexagonal phases and the  $\gamma$  and the 9R rhombohedral polytypes.

The GaSe structure is strongly dependent on the growth method and on the Iodine concentration. The structures observed in melt grown material are:

- only the  $\beta$  polytype in crystals grown without Iodine;
- the  $\epsilon$  and the  $\gamma$  phases in crystals with Iodine concentration ranging between 0.5 and 2.5 mg/cm<sup>3</sup>;
- the  $\epsilon$ ,  $\gamma$  and 9R in ingots with 3.5 mg/cm<sup>3</sup>;
- the  $\epsilon$ ,  $\gamma$ , 9R and 12R in ingots with 4 mg/cm<sup>3</sup>.

GaSe crystals obtained from the vapour with Iodine concentration between 0 and 2.5 mg/cm<sup>3</sup> show the presence of the  $\epsilon$  and  $\gamma$  structural modifications, while the material grown with 3mg/cm<sup>3</sup> Iodine concentration is made up of the  $\epsilon$ ,  $\gamma$  and 9R polytypes.

## 2. Reference

- [1] A.M. Mancini, G. Micocci and A. Rizzo,  
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