Acta Physica Academiae Scientiarum Hungaricae, 53 (1—2), pp. 133—141 (1982)

THE GROWTH AND TEXTURE STUDY OF GaSb INGOTS*

M. HÁRSY, F. KOLTAI, I. GYURÓ, T. GÖRÖG and E. LENDVAY

RESEARCH INSTITUTE FOR TECHNICAL PHYSICS, HUNGARIAN ACADEMY OF SCIENCES
1325 BUDAPEST, HUNGARY

GaSb was synthetized from Ga of 6N and Sb of 5N5 purity. After the synthesis the crystallization took place in Bridgman-type growth systems. Terrestrial and space experiments aboard Salyut-6 have been performed. In terrestrial experiments depending on the growth parameters (pulling rate, ampoule diameter, etc.) macro-, or polycrystalline ingots showing a characteristic texture have been formed. It has been observed that in wider ampoules boules of better quality have grown, the diameter of individual crystals ranging from 1—3 cm. In the space experiment a high-quality bicrystal has been formed. Examining the texture of terrestrial samples, the orientation of crystallites, the number of low and wide angle grain boundaries have been determined using electron channelling (EC) patterns.

1. Introduction

In the last few years GaSb has become one of the most attractive semiconducting materials. Apart from its optoelectronic application as laser diodes or detectors in the near infrared range [1—3], the single crystals of GaSb are excellent substrate materials for developing different ternary and quaternary layer structures. The GaSb, for instance, has a close lattice match with AlGaSb, AlGaAsSb and InGaAsSb. These hetero systems grown epitaxially onto GaSb substrates are used for photodetectors, LED and laser devices working in the visible and the near infrared regions of the spectrum [4—6].

The most essential requirement for these applications is the production of perfect single crystalline GaSb. To prepare usable GaSb crystals is, however, not a simple problem. Numerous publications describing different growth processes and aimed at improving the quality of GaSb crystals have been published, but the materials obtained so far often contain microscopic and macroscopic defects as well [7—11]. The crystals usually show twinning and also microfaceted growth is frequently observed. Boules pulled by the widely used Czochralski technique exhibit macroscopic heterogeneity of impurities due to the so-called "facet effect" [12].

In this paper we present some results of our program to study the growth properties of GaSb and if possible to improve the quality of crystals. Luckily we had a chance to perform a GaSb crystallization experiment during the first Soviet—Hungarian joint space flight in 1980. Some of the findings will also be discussed.

* Dedicated to Prof. I. Tarján on his 70th birthday.

2. Experimental part

The synthesis and the subsequent crystallization of GaSb samples have been carried out in a Bridgman-type vertical arrangement. The gallium and arsenic in a stoichiometric ratio were placed into a conically tipped quartz tube which was later sealed under vacuum. Heating the ampoule to a temperature slightly over 730 °C the reaction of the components was completed within an hour. After the synthesis the ampoule was lowered slowly along the decreasing temperature gradient of the furnace. The lowering rate varied between 0.3 and 18 mm/hour, and ampoules of different diameters (8—30 mm) and shapes were tried. Fig. 1 illustrates some of the ampoule shapes. The lengths of the ingots were 40—50 mm.

In the space experiment a polycrystalline ingot of a length of 39 mm and a diameter of 8 mm was melted, then pulled out with a rate of 0.188 mm/min to the cooler part of the tube furnace where the material gradually crystallized. The experimental set-up is demonstrated in Fig. 2.

For the investigation, the upper top of the ingot was removed, then the remaining part was cut to halves along its length. The flat surfaces were polished and etched in the 1 : 1 : 2 mixture of $HCl : H_2O_2 : H_2O$. The latter made the wide angle grain boundaries visible.

The fine structure measurements took place in JEOL JSM-35 type three lense Scanning Electron Microscope (SEM) using the Electron Channelling (EC) effect (Fig. 3).

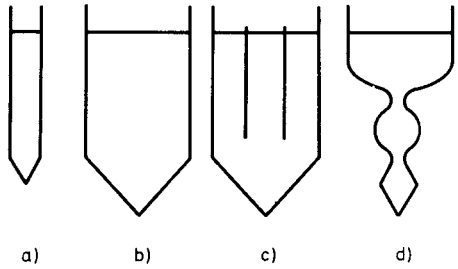

Fig. 1. Different ampoule shapes used for GaSb growths

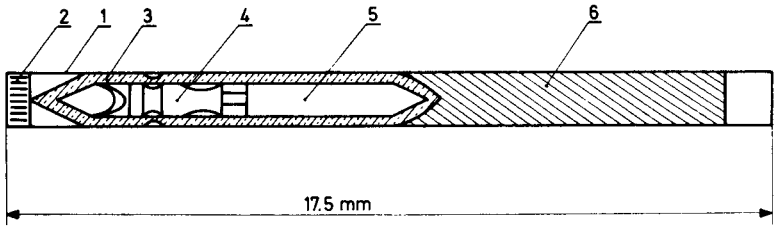

Fig. 2. GaSb space capsule. 1. Stainless steel tube, 2. screwed in cap, 3. quartz ampoule, 4. graphite spacer, 5. polycrystalline GaSb, 6. asbestos wool

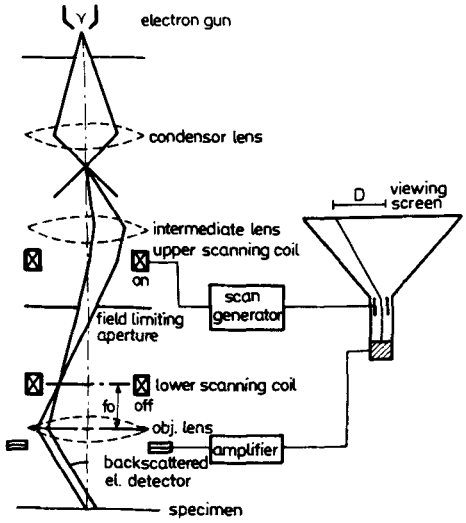

Fig. 3. EC measuring set-up

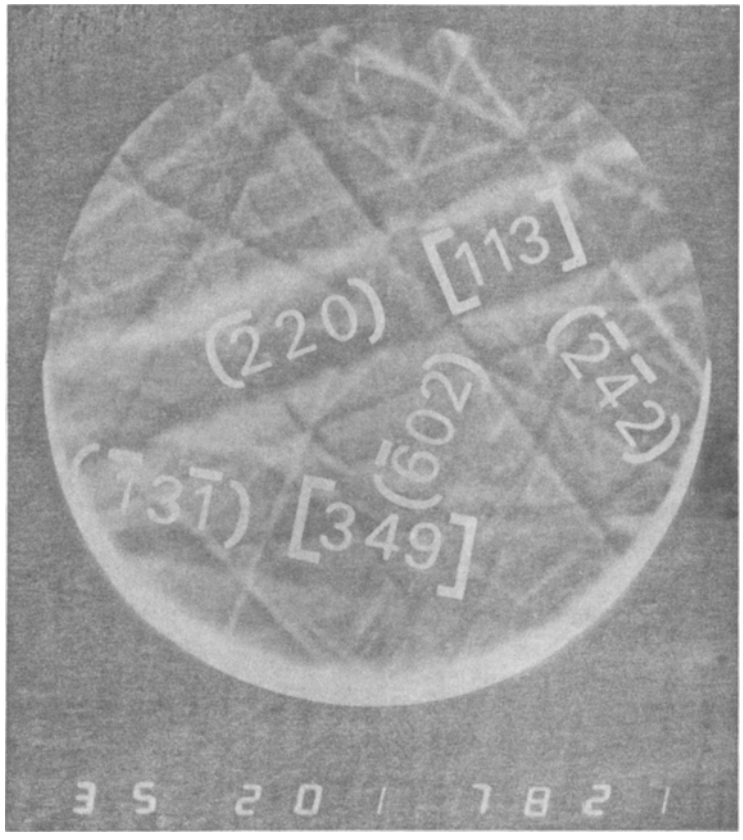

Fig. 4. A typical EC pattern

An EC pattern is formed when the electron beam impinges a small area of the sample, while the direction of the beam is altered in appr. 8° surroundings of the optical axis. Points of the viewing screen correspond to definite directions of the beam and a Kikuchi pattern like image consisting of white lines can be observed (Fig. 4). The brightness is proportional to the number of backscattered electrons, and their number is a function of the angle of incidence to the crystallographic planes. The cross-section of the Rutherford scattering is higher when the angle of incidence is somewhat smaller than the Bragg angle, and lower when it exceeds the Bragg angle.

The accelerating voltage and the beam current used were 35 kV and appr. 10^{-7} A, respectively. The diameter of the beam at the sample surface was 10—30 μm, therefore rather small areas could be studied. The crystallographic planes corresponding to the pairs of lines and bands were determined by a trial-and-error procedure, then the laboratory coordinates of the [001], [010] and [100] directions were computed. Using the orientation matrix composed from these data the laboratory indices can be converted to normal Miller indices or vice versa. Applying this computation, both the texture and the grain boundary properties could be examined.

3. Results and discussion

Figs 5—6 show some representative samples.

The ingots are solid and free of inclusions but the surface of terrestrial ones frequently contain semi-spherical depressions due to vacuum residues between the quartz wall and the molten material. The space sample shows a peculiar ridged surface which suggests that the crystallization was quite free of wall effects and slow fluid motions, not detectable under ordinary gravitational conditions, determine the shape of the growing interface [13].

The crystallites of the terrestrial ingots were elongated in some cases to lengths a hundred times their widths, and positioned more or less parallel to each other, along the ampoule length. Other samples consisted of only a few crystallites of dimensions near those of the ingots.

Moving the electron beam perpendicularly to the ingot length the changes in EC patterns indicated the individual grains, and in this manner the number of grain boundaries could be counted. Table I summarizes some growth conditions and boundary numbers found in selected samples. The Table shows that in wider ampoules the nucleation is lower. The sizes of individual grains grow with decreasing pulling rate and this effect is more significant for wider ampoules. It can be supposed that the wall effect and some kind of stress, arising when the cooling of the boule is not uniform, play an important role in propagating the nucleation. Sample VII shows a good example of stress effect (Fig. 7). In a D-type ampoule the diameter of the interface was alternatively changed during the growth process, consequently the heat transport conditions varied, too. Applying a slow lowering rate, similar to that of Sample III, many crystallites have

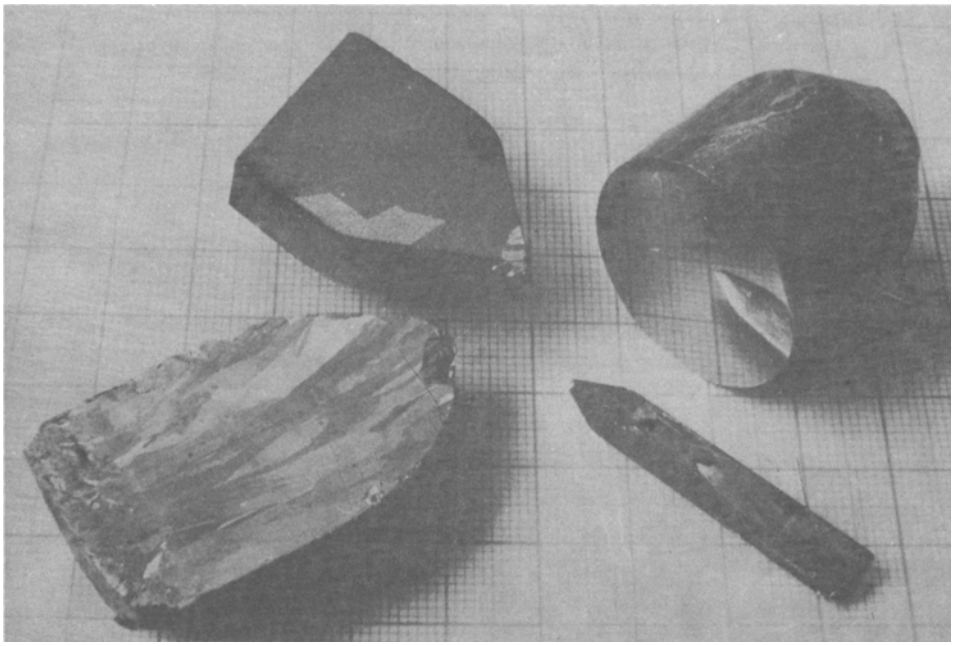

Fig. 5. Different GaSb ingots

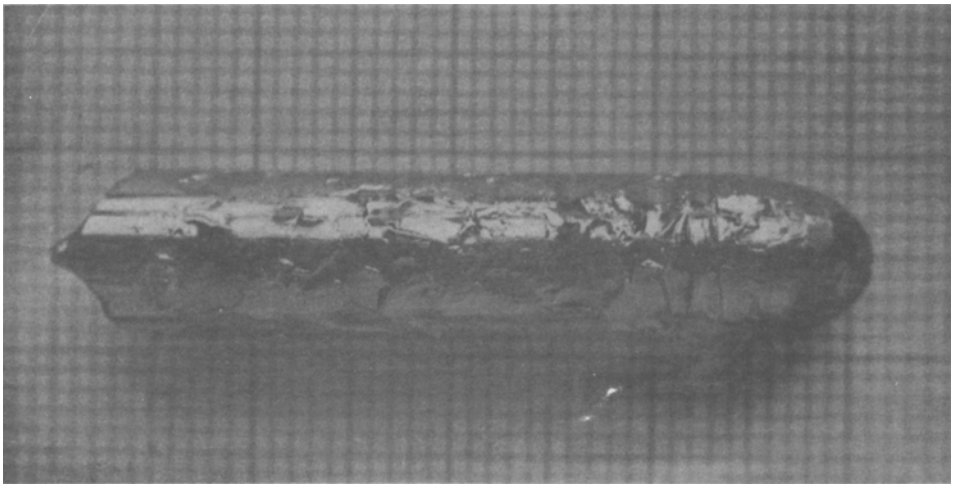

Fig. 6. Space-grown GaSb ingot

Table I
Growth parameters and number of boundaries/cm found perpendicularly to ingot length [14]

Sample	Diameter [mm]	Pulling rate [mm/h]	Boundaries [cm]		
			law angle	wide angle	total
I-3A	8	0.3	6	4	10
I-3B	8	18	20	10	30
II	28	18	16	8	24
III	28	3.6	7	0–1	7–8

formed, especially in the bulk of the balls, indicating the nucleation prone sections of the ingot.

The space sample gives an example to the contrary. In microgravity conditions the crystallization took place practically free of wall effect, resulting in a bicrystal with only three small twin lamellas penetrating into it (Fig. 8).

As has been already mentioned, the grains are elongated more or less parallel with the pulling direction. The chemically developed twin lamellas, in ingots consisting

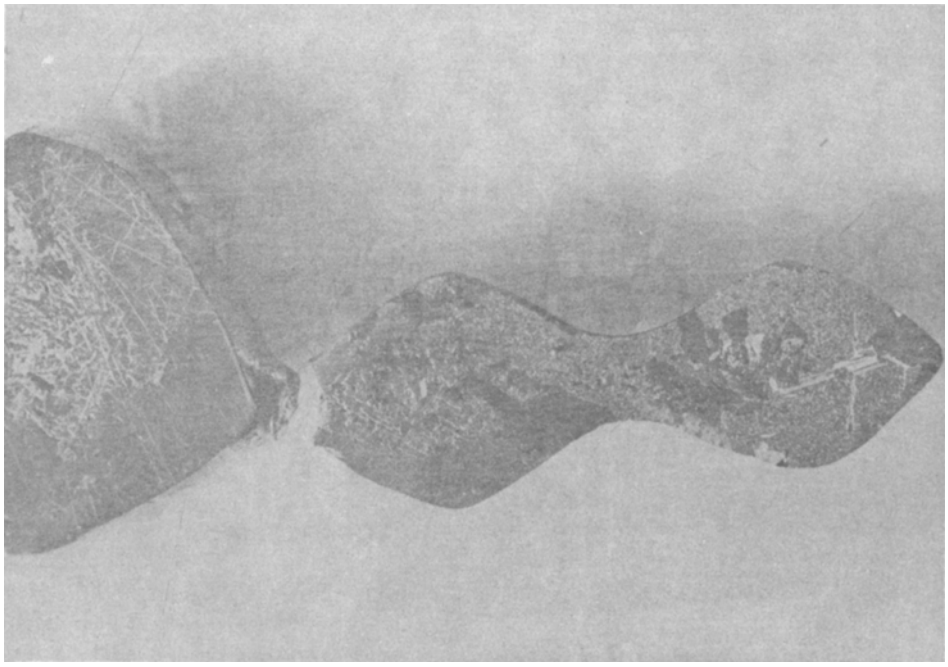

Fig. 7. Cross-section of Sample VII showing high density of grains in the bulk

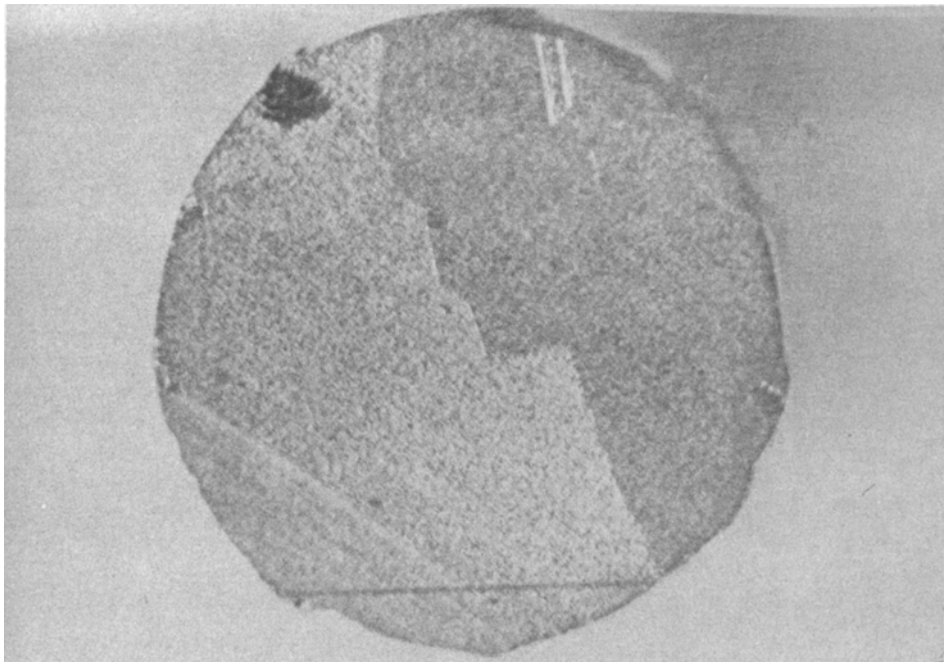

Fig. 8. The cross-section of space sample

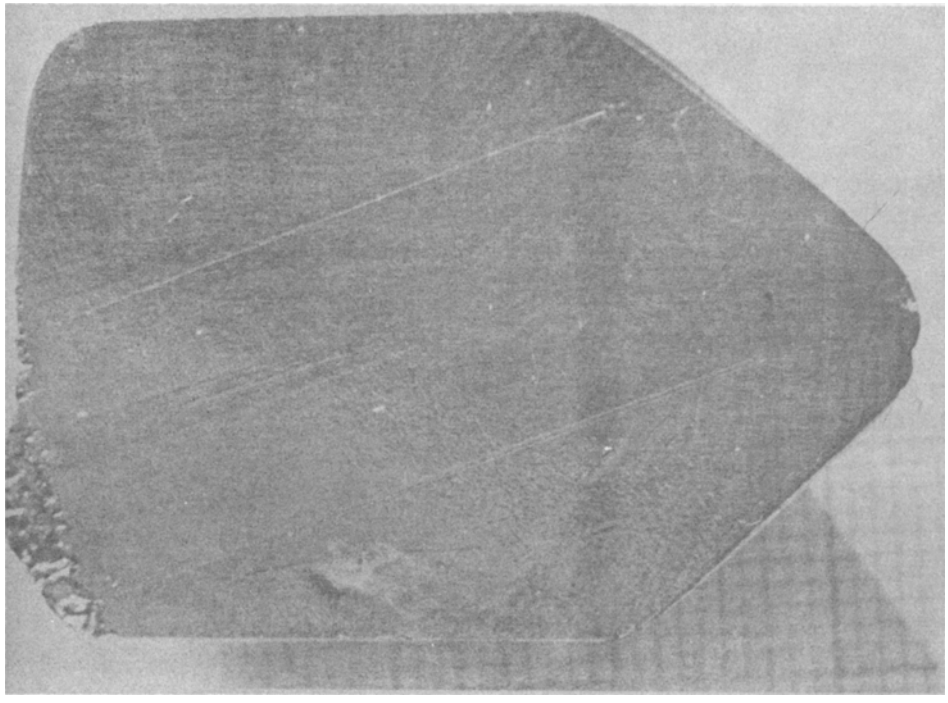

Fig. 9. Parallel twin lamellas in GaSb III

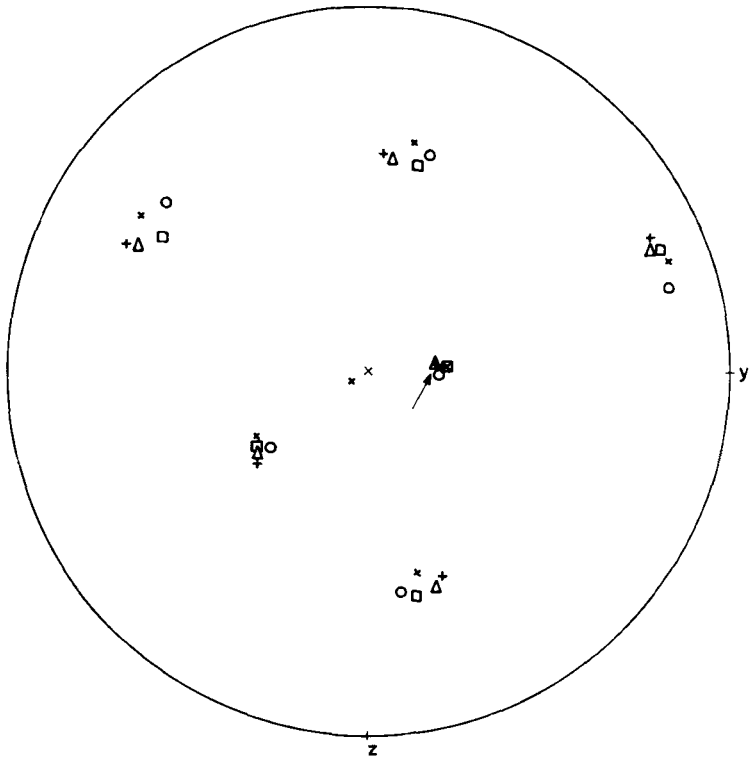

Fig. 10. Sample 1-3B. ⟨110⟩, directions of grains in the laboratory coordinate system

of only a few macroscopic crystallites, form clearly visible parallel lines (Fig. 9). According to our calculations, these lines indicate the ⟨110⟩ directions of the grains. If these ⟨110⟩ directions are placed into the stereographic projection of the laboratory coordinate system in which the centre point, i.e. the line rising perpendicularly upward from it represents the main axis of the ingot, they are grouped within a small circle near the centre. This means that the ingot has a definite texture in this direction.

In Sample VI, which contains numerous wide angle boundaries, the ⟨110⟩ directions of the grains are positioned along a circle, indicating that the individual crystallites are rotated randomly around their ⟨110⟩ axes. Those crystal sections in which only low angle boundaries can be found, show the same texture in ⟨110⟩ direction, but, in this case, their other crystallographic directions are also relatively close to each other, meaning that the crystallites are turned around the ⟨110⟩ axis by small angles (Fig. 10) only.

The deviation of textures from the ingot main axis is varied in different samples. In narrow ingots it was found about 5—7 degrees while the wider boules showed some 20 degrees deviation. More detailed texture analyses will be published later [15].

References

1. F. Capasso, M. B. Panish and S. Sumski, IEEE J. Quant. Electronics, QE-**17**, 273, 1981.
2. N. Kitamura, M. Kakehi, J. Shen and T. Wada, Jap. J. Appl. Phys., **20**, 995, 1981.
3. F. Capasso, M. B. Panish, S. Sumski and P. W. Foy, Appl. Phys. Letters, **36**, 165, 1980.
4. T. Sukegawa, T. Hiraguchi, A. Janaka and M. Hagino, Appl. Phys. Letters, **32**, 316, 1978.
5. L. M. Dolginov, L. V. Druzhinina, P. G. Elisev, A. N. Lapshin, M. G. Milvidskij and B. N. Sverdlov, Soviet J. Quantum Electr., **8**, 416, 1978.
6. H. Kano and K. Sugiyama, Electr. Letters, **16**, 146, 1980.
7. M. A. Dasevskij, G. V. Kukuladze and M. S. Mirgalovskaja, Soviet Inorg, Mater., **5**, 1141, 1969.
8. M. Kumagawa, J. Cryst. Growth, **44**, 35, 1979.
9. K. W. Benz and G. Miller, J. Cryst. Growth, **46**, 35, 1979.
10. T. Migauchi and H. Sonomura, Jap. J. Appl. Phys., **4**, 317, 1969.
11. G. Wolf, P. H. Keck and J. D. Broder, Phys. Rev., **94**, 753, 1954.
12. K. F. Hulme and J. B. Mullin, Phil. Mag., **4**, 1286, 1959.
13. E. Lendvay, M. Hársy, T. Görög, I. Pozsgai and J. Gyulai (to be published).
14. M. Hársy, T. Görög, E. Lendvay and F. Koltai, J. Cryst. Growth, **53**, 234, 1981.
15. F. Koltai, M. Hársy and E. Lendvay, (to be published).