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# Growth and microstructural characterization of SnSe-SnSe$_2$ composite

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As the Sn-Se eutectic solidification produces a lamellar structure, formed by SnSe and SnSe$_2$ compound, which are p and n semiconducting type, respectively, the SnSe-SnSe$_2$ *in situ* composite is a promising material to be used in photovoltaic device manufacturing. In this work, the Sn-Se alloys corresponding to the eutectic composition as well as to SnSe and SnSe$_2$ composition were processed by direction solidification at several solidification rates in a vertical Bridgman-Stockbarger crystal growth unit. The aim of the experiments was to evaluate the eutectic microstructure behavior as a function of directional solidification parameters. The obtained microstructures were analyzed by using X-ray diffraction and scanning electron and optical microscopies. The results obtained show that a very regular and aligned structure formed by the SnSe and SnSe$_2$ solid phase can be achieved. It was found that the presence of imperfections in the eutectic microstructure depends on the growth rate, and mainly, on the alloy homogenization process. *© 1999 Kluwer Academic Publishers*

## 1. Introduction

In the last few years, efforts have been undertaken in order to investigate the semiconducting behavior of transition metal selenides. Among these materials, tin monoselenide and tin diselenide exhibit several interesting features, including their electronic and optical properties, which could be useful in solar cells manufacturing [1–7]. The tin monoselenide shows an orthorhombic structure; It is a p-type semiconductor and its band gap is close to 1.0 eV [7–9]. On the other hand, the tin diselenide presents a hexagonal CdI$_2$-type crystal structure; It is an n-type semiconductor and its band gap is near 0.9 eV [1, 8, 9].

In an interesting paper, Bhatt *et al.* have analyzed some photovoltaic properties of thin films SnSe-SnSe$_2$ junctions [10]. Based on the electric characteristics of the SnSe and SnSe$_2$ compounds, they suggested that these materials could be useful in photovoltaic devices manufacturing. However, the manufacturing of thin film junctions of SnSe and SnSe$_2$, as well as any ordinary process of solar cell production may involve a number of complex and expensive procedures. Considering that a particular feature of the Sn-Se system is a eutectic transformation which, during solidification, may simultaneously produce SnSe and SnSe$_2$ phases, a promising alternative producing a low-priced and qualified solar cell or electronic devices, by employing a single growth process operation, is the use of directional solidification of the Sn-Se eutectic alloy [11–13].

Recently, directional solidification of eutectic alloys has been the subject of several theoretical and experimental studies. The motivation in performing these studies has been the feasibility of obtaining *in situ* composite materials directly from the liquid phase. Directional growth of eutectic composition alloys may lead to very periodic structure consisting of two or more coexisting solid phases [14–16]. A number of investigations have accentuated that the directional growth of eutectic alloys is an efficient technique in producing composite materials with interesting mechanical, electronic, optical, and magnetic properties [17]. In the Sn-Se eutectic growth, a lamellar structure is produced, where the SnSe and SnSe$_2$ solid phases grow side by side. Such a structure forms anisotype multijunction arrangements, which consist of alternate multilayers of p and n-type semiconducting composite. The possibility of using these type of materials in solar cell manufacturing was previously investigated by van Hoof and Albers [18].

Considering that to produce solar cells from Sn-Se eutectic alloys it is essential to obtain a very regular and aligned lamellar structure, the main objective of this work is to describe the preparation, growth and microstructure characterization of the *in situ* composite SnSe-SnSe$_2$.

## 2. Experimental

The aim of the experiments was to directionally grow and characterize the SnSe-SnSe$_2$ composite structure. The Sn-Se alloys were processed by directional solidification in order to lead to an aligned lamellar structure. To directionally solidify the samples, a vertical

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Bridgman-Stockbarger crystal growth equipment was employed. The vertical Bridgman-Stockbarger technique consists of gradually displacing a quartz ampoule containing the growth material from a hot section (high temperature) into a cold section (low temperature) of the heating unit. Such an operation allows one to control the thermal gradient ahead of the solid/liquid interface, the solidification rate, as well as the shape of the solid/liquid interface. The hot zone at the top and the cold zone below were made up of two transparent, gold-deposited heating units and separated by insulation. The heating elements were obtained from sheathed coax as a rigid coil.

In addition to the eutectic composition, samples associated with the SnSe and $SnSe_2$ compositions were prepared in order to compare the crystal structure characterization results obtained from the eutectic microstructure with results obtained from characterization of the SnSe and $SnSe_2$ compounds which were individually grown. The samples were obtained by weighing a correct quantity of 99.99% pure Se pellets supplied by the Aldrich Chemical Company, Inc. and of 99.999% pure Sn shot supplied by Johnson Matthey Chemicals Limited, corresponding to three compositions: 50.96 wt % Se for eutectic samples; 40.00 wt % Se for SnSe samples and 58.00 wt % Se for $SnSe_2$ samples. Quartz tubes were sealed at one end and employed as the material for encapsulating the materials. These tubes containing the Sn-Se alloy were purged with argon and sealed under a vacuum of $10^{-5}$ Torr. The quartz tubes were 0.8 cm ID × 1.0 cm OD and 55.0 cm long. Before performing the directional growth, to achieve a regular eutectic growth, the Sn-Se alloys were well-homogenized by processing the growth material in a rocking furnace at 860 °C for four hours. After homogenization, the samples were transferred to the crystal growth apparatus for the directional solidification processing.

The eutectic ingots 6.0 cm in length and 0.8 cm in diameter were directionally solidified by pulling down the samples from the hot to cold zone at displacing rates ranging from 0.47 cm/h to 3.07 cm/h. The directional growth was performed with the hot zone set at a temperature of 850 °C, while the cold zone was fixed at 150 °C. On the other hand, to obtain SnSe and $SnSe_2$ single crystals, in both growth experiments, the same mentioned ampoule type was employed, the growth rate was set at 1.0 cm/h, and the temperature of the hot and cold zones were set at 900 and 150 °C, respectively. These temperatures resulted in a thermal gradient at the solid/liquid interface ranging from 60 to 80 °C/cm.

The microstructure was characterized by observing cross and longitudinal sections at several positions along the ingot. The ingot sections were prepared with wax on a brass matrix. Initially, the pieces were mechanically polished and then, chemically polished in a solution of 100 ml of absolute ethanol and 2 g of iodine. The microstructures were analyzed by using transmission electron (TEM), scanning electron (SEM) and optical microscopies, as well as powder X-ray diffraction technique. In order to determine the lamellar spacings, on each section, the distance of a certain number lamellae pairs was measured in a direction parallel to the solid/liquid interface.

## 3. Results and discussion

The use of quartz ampoules to grow the Sn-Se eutectic alloy was found to be an appropriate option, since no reaction between the quartz walls and the sample was detected. Initially, to examine the efficiency of using a rocking furnace in the alloy homogenization process, two types of alloy preparation procedure were utilized: eutectic samples homogenized in the rocking furnace at 860 °C for four hours and eutectic samples homogenized by just keeping them at 860 °C for four hours. After directionally solidifying these samples, the resultant microstructures revealed that the use of the rocking technique is essential in preparing the Sn-Se eutectic alloy, since the intensity of imperfections was much smaller in the samples processed in the rocking furnace. These samples were also characterized by using energy dispersive X-ray analysis (EDX/SEM), which confirmed that the homogenization process in a rocking furnace is able to produce a very uniform composition ingot.

Examination of the Sn-Se phase diagram suggests that the Sn-Se eutectic microstructure belongs to the lamellar type, since several investigations indicate that when the volume fractions of the solid phases are close to 0.5, the solidification leads to lamellar morphology. Experimental evidence obtained from optical microscopy confirmed such a hypothesis. Fig. 1 presents directionally solidified Sn-Se eutectic microstructures obtained at several growth conditions. Under optical microscopy, the black phase is richer in selenium ($SnSe_2$), while the gray phase is richer in tin (SnSe).

As the eutectic microstructure depends on the growth parameters, it is fundamental to understand the effect of the operational conditions on the solidification phenomenon, since it permits predicting the resultant microstructure. In order to obtain an aligned eutectic microstructure, very controlled growth conditions and a well defined alloy composition are essential. However, a regular eutectic alloy under directional solidification, may occasionally produce an unexpected structure, like cellular or dendritic morphology, or a microstructure with a high intensity of defects, like eutectic grains or lamellar terminations. In this work, the nature and intensity of these defects were related to the growth rate and to the alloy composition. Growth experiments of a slightly off-eutectic composition sample produce a very irregular microstructure formed by primary phase surrounded by the SnSe-$SnSe_2$ eutectic. On the other hand, the eutectic grain size decreased, and the amount of lamellar terminations increased with an increase in the growth rate.

In eutectic growth where high entropy of fusion phases are formed, as in the case of SnSe and $SnSe_2$ compounds [19], we expect to achieve an irregular eutectic structure, since the diffusion-controlled growth is not invariably likely. However, the Sn-Se eutectic growth led to a very regular morphology, nevertheless the microstructure presented a clear lamellar spacing selection problem, which is probably connected to

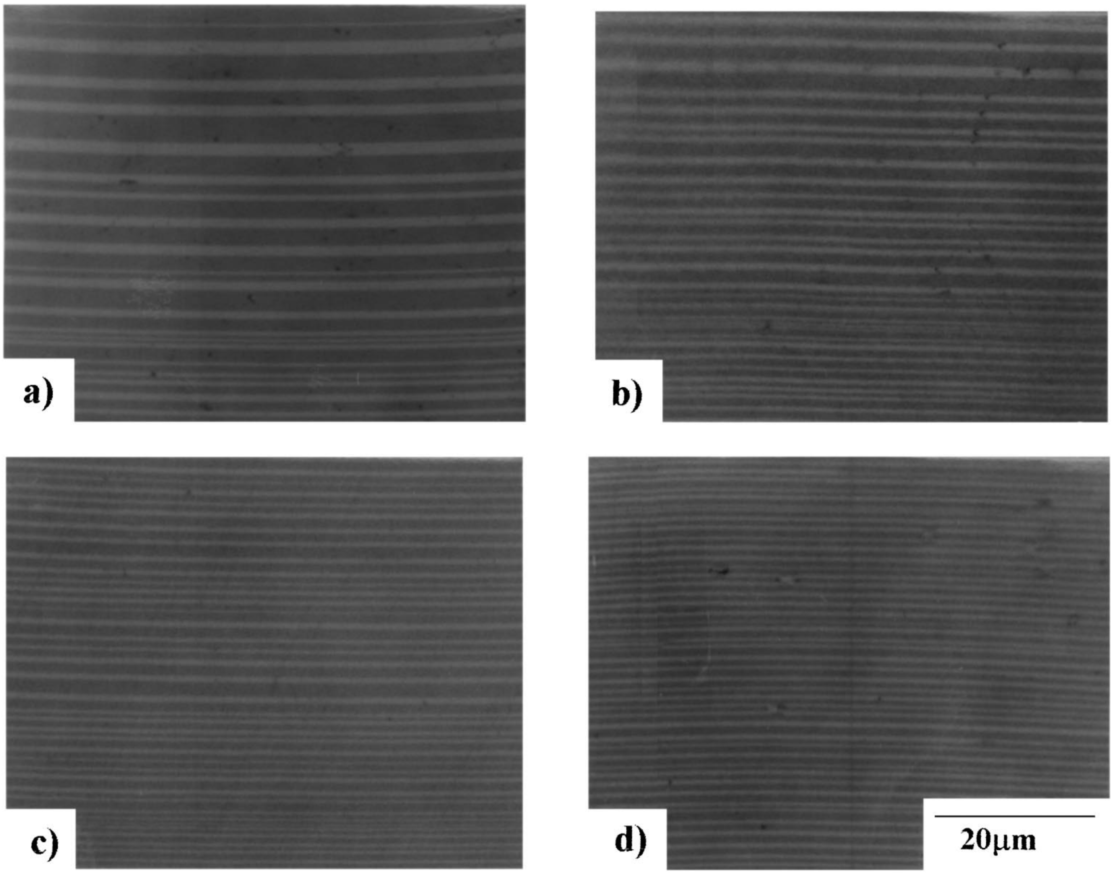

*Figure 1* Optical photographs of the directionally solidified Sn-Se eutectic microstructure obtained at different growth rates: (a) 0.47; (b) 1.54; (c) 2.03 and (d) 3.07 cm/h.

difficulties in the branching phenomenon. Applying a fixed solidification rate, it was found that the individual lamellar spacings are distributed over a large range of values. This event suggests that the lamellar spacing selection in the SnSe-$SnSe_2$ eutectic growth is not narrow and a range of spacing values is obtained for a particular growth rate. However, an increase in the growth rate, apparently led to a more efficient lamellar selection, since the lamellar structure is more uniform at higher growth rates.

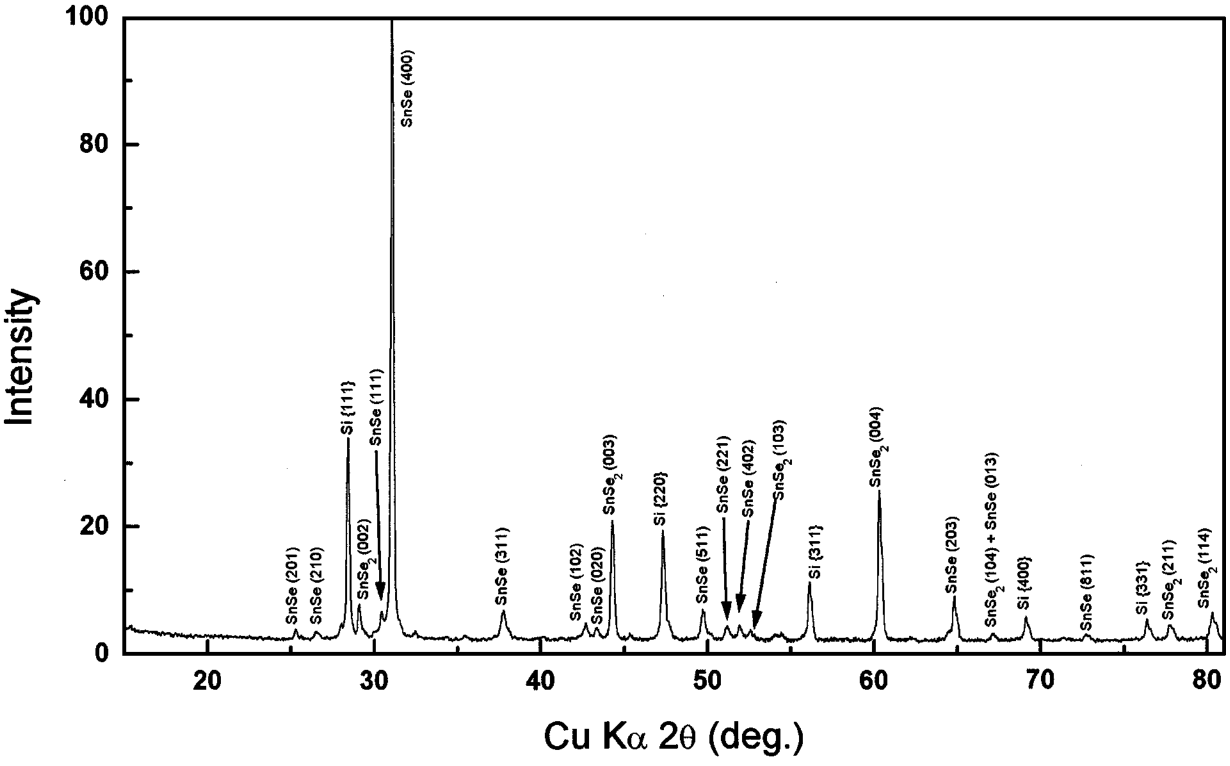

*Figure 2* Powder X-ray diffraction pattern of the SnSe-$SnSe_2$ eutectic.

By examining defect free sections in the eutectic microstructure, a relationship between eutectic microstructure scale and growth conditions was determined as $V\lambda^2 = 5.0 \times 10^{-8}$ $cm^3/h$. To evaluate the eutectic spacings, radial views were used. Despite the fact that SnSe and $SnSe_2$ are not expected to present non-faceted growth, and since they have high entropies of fusion, the eutectic growth behavior was comparable to a diffusion-controlled one. In the SnSe-$SnSe_2$ growth, a decrease in the solidification rate resulted in an increase in the spacings, as predicted by Jackson and Hunt theory [20].

In order to check the solid phases characteristics, their crystal symmetry and their lattice constants in the directionally solidified eutectic samples, a X-ray powder diffraction method was utilized. In this case, a small amount of silicon (99.999% purity) was added to the samples in order to provide a reference pattern. As shown in Fig. 2, the X-ray difractograms indicated the presence of the SnSe and $SnSe_2$ solid phases. The directional growth of samples corresponding to the SnSe and $SnSe_2$ compositions resulted in ingots with a few grain boundaries. The grains were aligned in the direction parallel to the heat flux. The X-ray results allow one to affirm that the eutectic SnSe-$SnSe_2$ diffractogram is a result of the perfect association of their solid phases difractograms. Also, considering the limitations of the X-ray diffraction analysis, the solid solubilities were found to be very small. By using electron diffraction analyses provided by TEM and the X-ray diffraction analysis, it was confirmed that the SnSe compound crystal symmetry is orthorhombic with lattice constants $a = 1.151$ nm, $b = 0.417$ nm and $c = 0.443$ nm. The $SnSe_2$ compound presents a hexagonal structure, with $a = 0.382$ nm and $c = 0.6138$ nm. Fig. 3 shows transmission electron micrographs of SnSe and $SnSe_2$

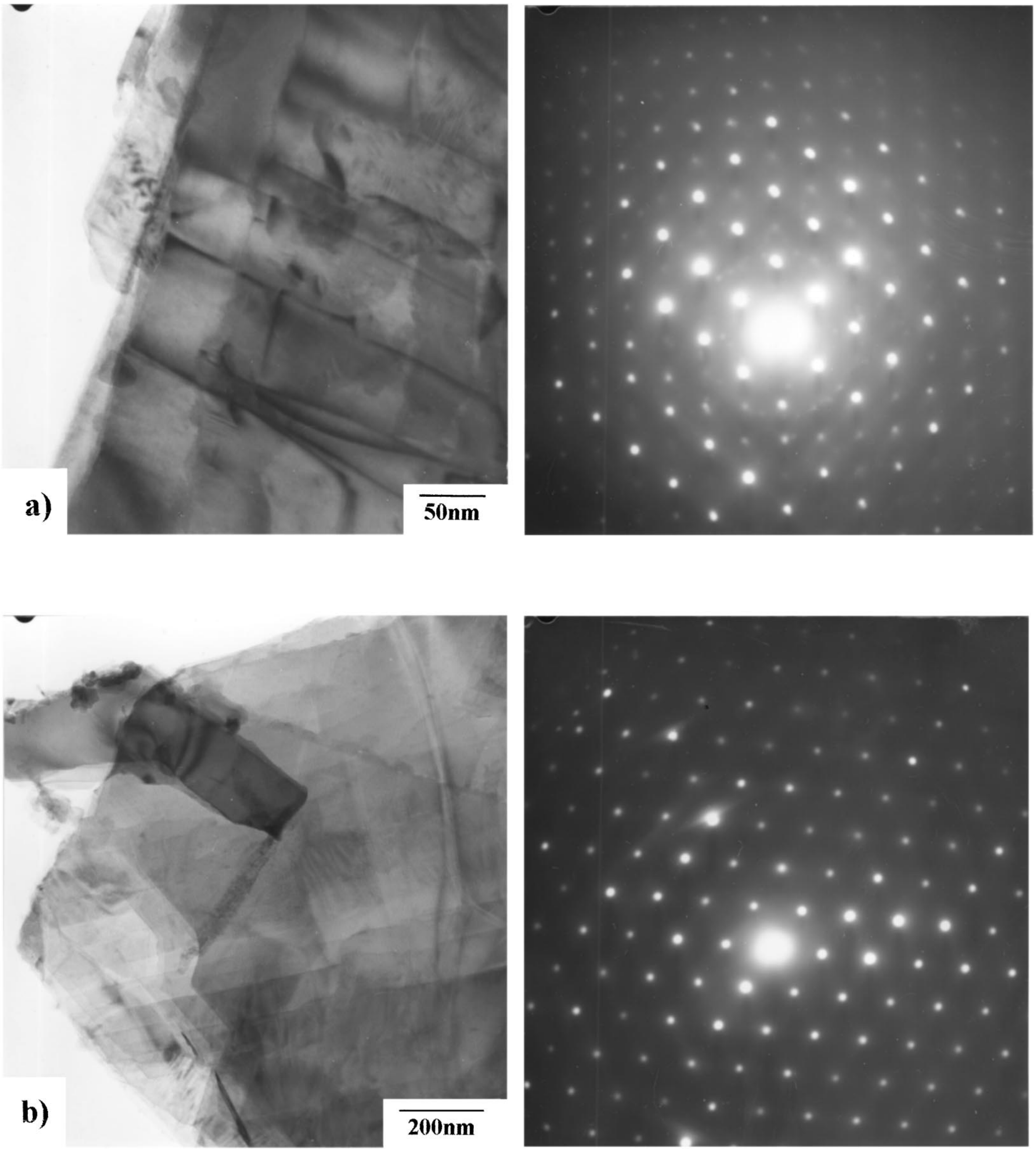

*Figure 3* Electron micrograph and electron diffraction pattern of (a) SnSe and (b) $SnSe_2$ compounds.

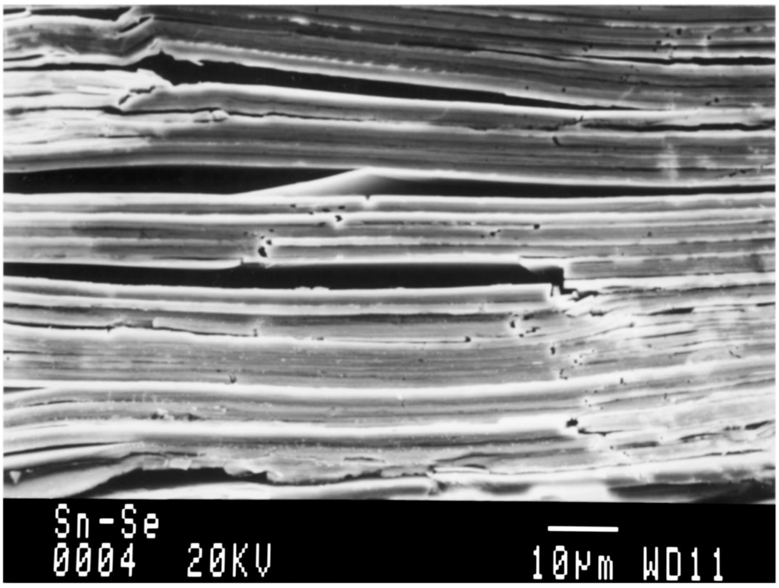

*Figure 4* Eutectic microstructure showing cleavage planes after deformation.

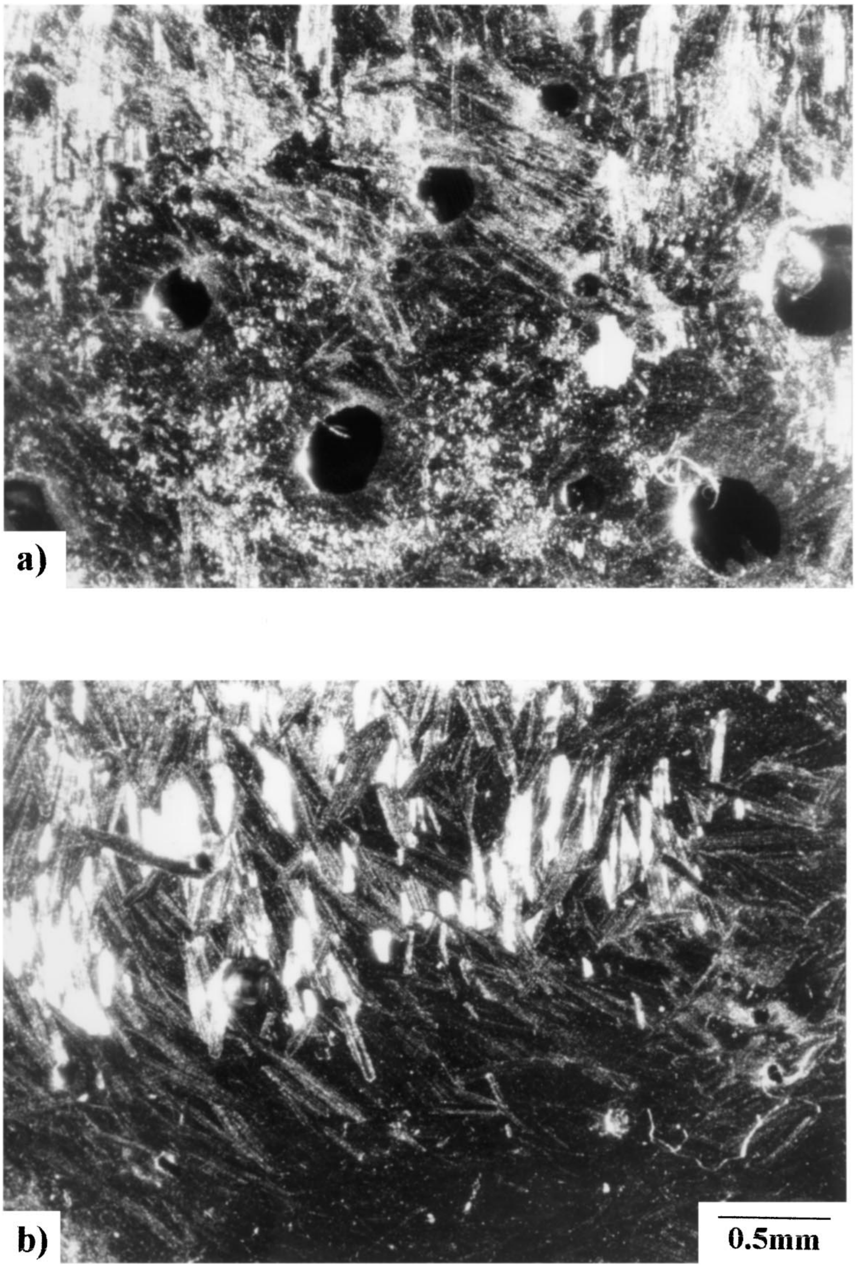

*Figure 5* Porosities in a cross section of directionally solidified Sn-Se eutectic ingots: (a) Growth without $B_2O_3$ and (b) Growth with $B_2O_3$.

compounds. In Fig. 3a, the beam is oriented with the direction [001], and the diffraction pattern shows an orthorhombic structure. In the $SnSe_2$ examination, as shown in Fig. 3b, the beam is also parallel to the direction [001], and the obtained diffraction pattern suggest that such a compound is of the hexagonal type crystal structure. In the eutectic structure, both compounds grow side by side having the SnSe plane (001) parallel to the $SnSe_2$ plane (001). Also, the cleavage plane of both SnSe and $SnSe_2$ compounds is the family {001}, as observed in Fig. 4. Such a figure shows a deformed region in the eutectic structure.

In all experiments related to directional growth of the eutectic alloy, an intriguing phenomenon was observed. The grown samples presented a high degree of porosity, as shown in Fig. 5a, which was apparently due to the evaporation of constituents during the solidification. As the heater of the Bridgman-Stockbarger crystal growth unit becomes almost transparent at temperatures above 800 °C, bubbles moving through the melt phase were clearly observed and they were unquestionably related to these porosities. These defects are probably due to selenium sublimation, as well as a result of the presence of selenium oxides ($SeO_2$ and $SeO_3$) in the samples. As both oxides are not stable at the eutectic temperature, they could lead to bubbles nucleation, and hence, to porosities in the ingots.

To avoid the bubble formation and hence, the porosity development, a different growth experiment was tried. As the selenium presents easy volatilization, the same quartz ampoule described before was loaded with Sn-Se eutectic composition alloy (50.99 wt % Se), which was previously homogenized in a rocking furnace, and sealed under $10^{-5}$ Torr vacuum using $B_2O_3$ (99.99% purity) as a liquid encapsulant material. The $B_2O_3$ is frequently utilized in the GaAs growth. In spite of the fact that $B_2O_3$ was not entirely impermeable to the bubbles, the use of such an encapsulant material led to ingots with reduced level of porosities, as shown in Fig. 5b.

## 4. Conclusions

Sn-Se alloys of eutectic composition, as well as SnSe and $SnSe_2$ compositions were directionally solidified in Bridgman-Stockbarger equipment and a microstructure characterization was carried out. For growth rate varying from 0.47 to 3.07 cm/h, very regular and aligned lamellar eutectic structures were obtained. However, such eutectic growth presented lamellar spacing selection problems. The directionally solidified eutectic samples showed a high degree of porosity, which is probably related to selenium and their oxides sublimation. The X-ray diffraction analysis showed that the eutectic microstructure solid phases have the same crystal characteristics of the individual SnSe and $SnSe_2$ structures. In spite of the utilization of several growth rate values, the eutectic morphology remained lamellar and a relationship between growth rate and lamellar spacing was evaluated. The electron diffraction analyses confirms that the SnSe and $SnSe_2$ compounds have, respectively, orthorhombic and hexagonal crystal structures.

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