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Section 2: Organic materials *INVITED*

HYBRID ORGANIC-INORGANIC CRYSTALS FOR QUADRATIC NONLINEAR OPTICS

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A route of crystal engineering aiming at the production of efficient quadratic nonlinear optical (NLO) crystals is based on chromophores anchored onto inorganic host matrices by hydrogen bonds and leads to non-centrosymmetric frameworks. These hybrid organic-inorganic salts try to combine the advantages of organic crystals (high NLO efficiency) and those of the inorganic materials (good stability, wide transparency range). We have undertaken the crystal growth from solution of the more promising salts of 2-amino-5-nitropyridinium: the phosphate, arsenate and phosphate- arsenate solid solution. Several growth methods have been used close to room temperature (30-50°C) such as the typical temperature lowering one. In addition, we developed an original vertical temperature gradient technique. This leads to the elaboration of large and high quality crystals suitable for NLO devices. These resulting crystals exhibit a better stability than those of corresponding molecular organic phases and high NLO efficiencies. Another important advantage of these organic-inorganic materials is the opportunity of solid solution existences through the mineral sub-networks. The evolution of the composition in a solid solution allows to adjust several linear and nonlinear optical parameters. The optical indices evolution allows to carry out wave-guide devices from crystal growth epitaxy. This is verified for the full 2-amino-5-nitropyridinium dihydrogenphosphate-arsenate (2A5NPDP-2A5NPDAs) solid solution.

Keywords: Hybrid crystals, Solution growth, Liquid phase epitaxy, Quadratic nonlinear optics

1. Introduction

Despite very large nonlinear optical (NLO) responses (up to two order of magnitude higher than those of inorganic compounds), organic molecular crystals have a very limited field of industrial applications due to their low stability (thermal, mechanical or chemical) and their reduced transparency window compared with those of inorganic crystals. To realize a material with high nonlinear optical efficiency in the visible and near IR region associated with convenient stability, a new family of hybrid organic-inorganic crystals has been developed in our laboratory [1-3].

These hybrid compounds are the result of a crystal engineering strategy aiming at the production of very cohesive, non-centrosymetric packing of organic polar chromophores by anchoring them onto inorganic matrices. The combination of ionic, optically active chromophores with suitable inorganic counterparts leads to acentric three-dimensional networks of short hydrogen bonds with enhanced stability. The resulting hybrid crystal structures represent a first compromise between the advantages of the organic phases (nonlinear response due to their high electron hyperpolarizabilities) and inorganic compounds (good stability). The organic cation mainly used in this crystal engineering was the 2-amino-5-nitropyridinium ($2A5NP^+$), 60% of the hybrid structures build with that chromophore were non-centrosymmetric. For instance several typical salts of 2-amino-5-nitropyridinium can be listed: dihydrogenphosphate [4], dihydrogenarsenate [5], L-hydrogentartrate [6], chloride and bromide [7]. These salts present high nonlinear coefficients ($d_{ij}(0.532\ \mu m) \approx 10\text{-}40$ pm/V [8-10]), transparency ranges extending over all the visible and near IR regions (0.4-1.8 μm) as well as improved stability compared to the corresponding organic molecular crystal (2A5NP): the thermal stability of 2A5NP is less than 100ºC while that of hybrid structures ranges from 160 to 200ºC.

An additional advantage of these hybrid phases over organic molecular crystals is the existence of solid solutions by chemical substitutions in the inorganic sub-network. Examples of such substitutions are $H_2PO_4^- \leftrightarrow H_2AsO_4^-$ or $Cl^- \leftrightarrow Br^-$. That possibility to continuously modify the chemical composition in the solid solution is a convenient way to adjust several linear and nonlinear optical properties of the material such as the refractive indices, the phase matching directions and the efficiency of second harmonic generation. Moreover, the modification of the refractive indices can be used to realize wave-guide structures through the epitaxy of a solid solution composition on a substrate whose composition of the same system exhibits lower refractive indices.

The hybrid solid solution we studied more particularly is the 2-amino-5-nitropyridinium dihydrogenphosphate/dihydrogenarsenate system ($2A5NPDP_{(1-x)}As_x$ with $0 \leq x \leq 1$, Fig. 1). Indeed, for that particular solid solution, the inorganic sub-network, made of $H_2XO_4^-$ (X=P, As) planes, can influence the optical properties of the material in two ways. On one hand, by a direct contribution to the nonlinear coefficients: $H_2XO_4^-$ tetrahedra are at the origin of the nonlinear response of several inorganic salts such as KH_2PO_4, $NH_4H_2PO_4$, RbH_2PO_4 for instance [11]. On the other hand, the inorganic anions modify the electronic states of the organic chromophore [12]. In addition, chemical composition changes in the solid solution do not induce important modification of the cell parameters and lead thus to a favorable case for growth epitaxy. For all these reasons, the crystal growth of the $2A5NPDP_{(1-x)}As_x$ solid solution was studied to determine the influence of the composition on the optical properties and to investigate the possibility to succeed growth epitaxy.

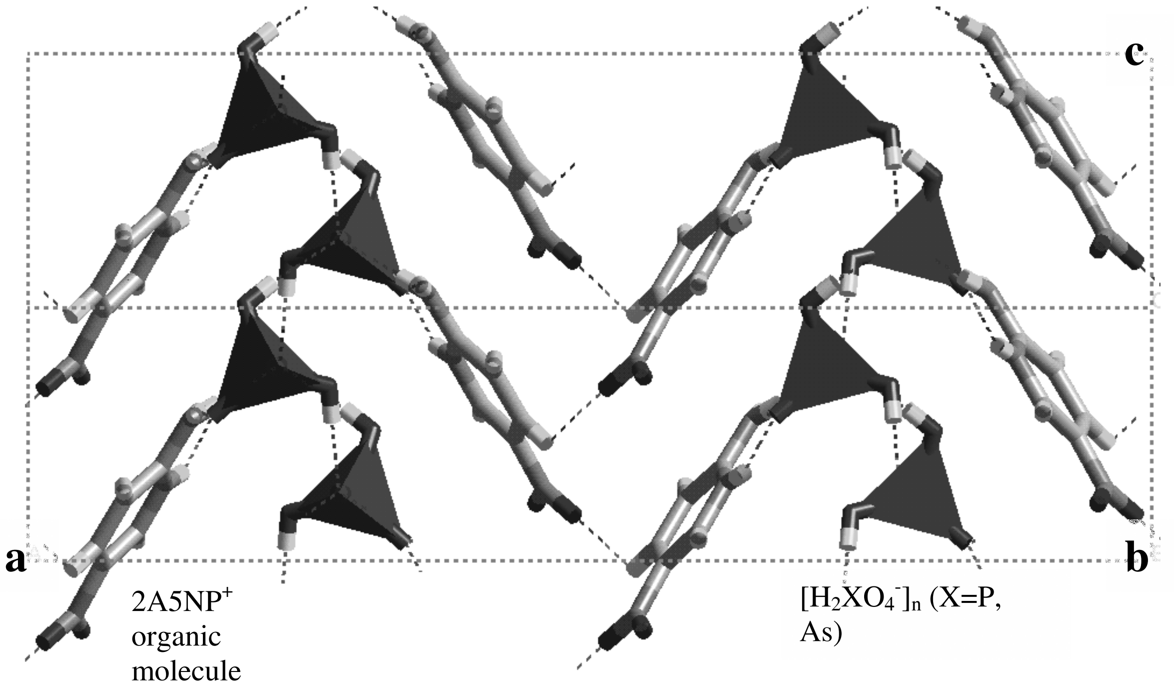


Fig. 1. Crystal structure of the $2A5NPDP_{(1-x)}As_x$ solid solution (space group P $na2_1$), projection along b, c is vertical.

2. Experiments

2.1 Crystal growth in solution

The decomposition before melting of these hybrid salts prompted us to carry out their crystal growth in solution. The selected solvents were the acid mixtures H_3PO_4/H_3AsO_4 (3-4M) corresponding to the salt or acetic acid (16.5M). The later one was selected to reach lower pH values (pH $\approx$ 0) in order to stabilize the organic chromophore in solution and to avoid its oxidation. The extreme compositions of the solid solution (2A5NPDP and 2A5NPDAs) were grown by a typical Temperature Lowering (TL) method involving a very high stability (T±0.002°C) in order to have a good growth stability [13]. The temperatures were close to room temperature (50 to 35°C) and lowering rate was 0.1-0.2°C/day on average. Due to the preferential deposition of phosphate anions, compared to arsenate ones, on the $2A5NPDP_{(1-x)}As_x$ crystals, a temperature gradient method had to be used to grow the intermediate compositions ($0 < x < 1$) of the solid solution. The nutrient of the desired composition is placed in the hotter part (dissolution zone) of the reactor while the seeds are located in the cooler part (growth zone). A presentation of this vertical gradient reactor is given elsewhere [14]. The temperature difference between the two parts was $\Delta T \approx$ 2-3°C and the temperature stability was about T±0.01°C.

2.2 Liquid Phase Epitaxy (LPE)

As for bulk crystal growth, LPE experiments were carried out in solution using the dipping technique. Substrates are dipped for a given period of time in a supersaturated solution of the composition to be deposited. In our case, relative supersaturations between $\sigma = 1.5\%$ and $\sigma = 6\%$ were created by keeping the temperature of the growth solution below the solubility equilibrium using the temperature lowering reactor [13]. A dummy substrate was first placed in the solution to determine when the supersaturation is stabilized. Once dipped, the substrates were rotated in the solution (about 20-30 rpm) in order to avoid concentration gradients close to the surface and two-dimensional nucleation. In order to reduce the turbulences in the solution, which would be detrimental to the crystal quality of the epitaxial layer, the substrates were oriented horizontally, with their surface in the rotation plan. Since the substrate must have lower refractive indices than the guiding layer, slices of 2A5NPDP crystals (lowest refractive indices of the solid solution) with different orientations (100) and (010) were used as substrates and two different compositions were deposited: $2A5NPDP_{0.8}As_{0.2}$ and $2A5NPDP_{0.5}As_{0.5}$.

One of the main conditions to obtain good wave-guide from LPE is to obtain sharp and flat interfaces (air - epitaxial layer - substrate). LPE is not very convenient for this purpose. Indeed, the substrates have to be kept above the solution while the supersaturation is established. During this first step, the solvent vapor slightly dissolves the substrate leading to a rough substrate - layer interface. Moreover, when the substrate is removed from the solution, a thin layer of the growth solution remains by capilarity on the epitaxial deposit leading to uncontrolled residual growth. The roughness of the two interfaces can lead to losses in the wave-guide making it useless. In addition, the roughness of the air - substrate interface can inhibit the light injection in the layer by reducing the quality of the optical contact between the wave-guide surface and the prism used to couple it with the light source. We have overcome these two difficulties by adding a layer of mineral oil above the growth solution. This oil was selected because it is not miscible with the aqueous growth solution and it does not dissolve the $2A5NPDP_{(1-x)}As_x$ hybrid crystals. Thus, the substrates could be kept over the solution for extended periods of time without any surface dissolution. In addition, when the substrates are slowly removed from the solution, the epitaxial layers are completely cleared of the solution which was replaced by a thin film of oil which stop suddenly the epitaxial growth.

3. Results

3.1 Crystal growth in solution

Using the temperature lowering and temperature gradient methods, large single crystals were successfully grown for several compositions of the solid solution: $2A5NPDP_{(1-x)}As_x$ with x = 0, 0.2, 0.4, 0.6, 0.8, 1 (Fig. 2a). The quality of the crystals was controlled by X-ray diffraction topography showing that both growth techniques lead to high quality crystals with low dislocation density [15]. The crystals of all the above compositions presented a similar stick shaped morphology, which is consistent with their isomorphous structure (Fig. 2b). Such bulky morphology is convenient for the preparation of optical devices. It is a direct consequence of the three-dimensional H-bond network obtained by combining the organic chromophore with the inorganic counterpart and represents an additional advantage of hybrid structures over organic molecular crystals. For the intermediate compositions of the solid solution, X-ray fluorescence was used to measure the As/P ratio in the crystals. This ratio was found constant all along the elongated axis of the crystals (Fig. 3) demonstrating that the temperature gradient method is a good way of growing homogeneous crystals despite the preferential deposition of the phosphate ions referred to the arsenates ones.

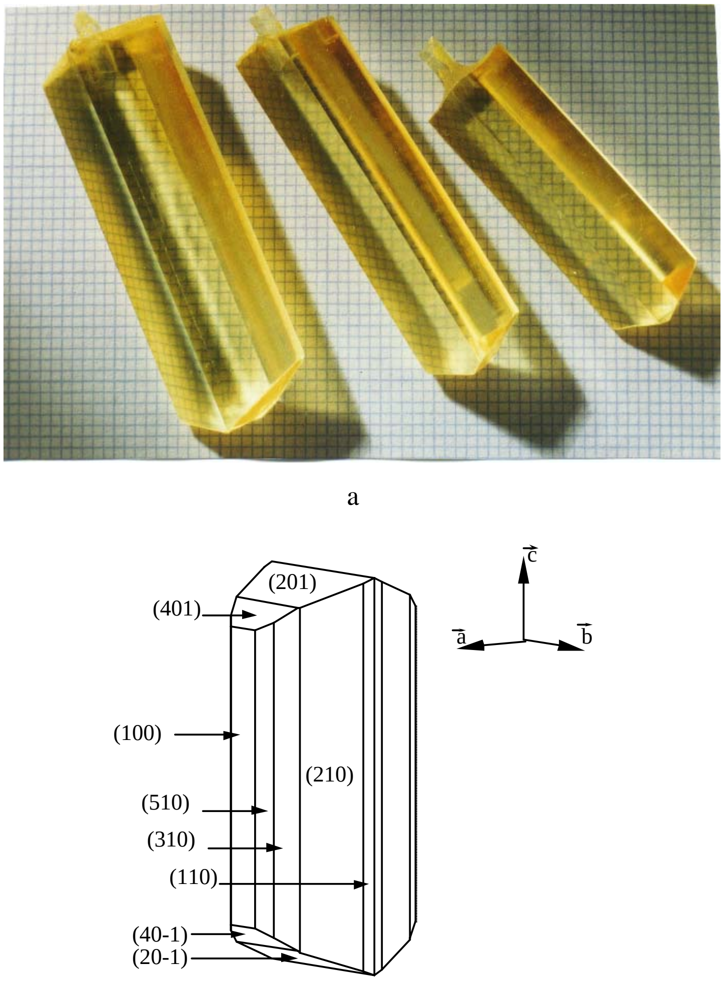


Fig. 2. (a) Single crystals of the $2A5NPDP_{(1-x)}As_x$ solid solution, the grid show millimeters, (b) Experimental morphology.

A standard procedure to grow large crystals of several cm^3 is to use previously grown crystals as seeds and particularly (001) crystal plates as crystals are elongated along the c-axis. In order to reduce the time necessary to obtain large single crystals of all the $2A5NPDP_{(1-x)}As_x$ compositions, we attempted to use the largest seeds of one composition to grow crystals of a neighboring composition. For instance, 2A5NPDP crystals of a few mm^3 in size were used to grow $2A5NPDP_{0.8}As_{0.2}$ crystals. These first successful experiments on growth epitaxy prompted us then to carry out other LPE experiments.

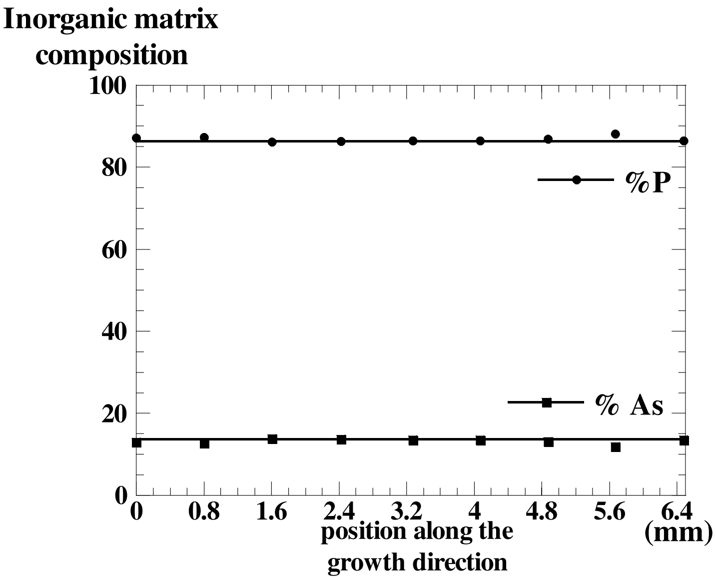


Fig. 3. X-ray fluorescence measurement of the mineral matrix composition along the favored growth direction (c - axis) of the crystal for an intermediate composition of the $2A5NPDP_{(1-x)}As_x$ solid solution (x = 0.13) grown by temperature gradient method.

3.2 Liquid phase epitaxy

To insure a maximum confinement of the optical wave, the layer forming the guide must have refractive indices significantly higher than those of the substrate ($\Delta n \geq 10^{-2}$). In the case of the $2A5NPDP_{(1-x)}As_x$ solid solution, the three principal refractive indices increase as a function of the As content. For this reason, we attempted to deposit layers with As content has high has possible onto 2A5NPDP substrates. However, when the As content is increased, it also increases the cell parameters mismatch between the layer and the substrate. Hence, a compromise has to be found between a high difference in refractive indices and a low cell parameters mismatch. That is the reason why the layer of highest As content we attempted to deposit on a 2A5NPDP substrate was $2A5NPDP_{0.5}As_{0.5}$. Fig. 4 presents such a layer deposited on a (100) 2A5NPDP substrate observed by scanning electron microscopy. One can see that in spite of cell parameters mismatches of $\frac{\Delta b}{b} = 0.79\%$ and $\frac{\Delta c}{c} = 0.97\%$, an 80 μm thick layer could be deposited on the substrate. This layer was further characterized by X-ray diffraction on a two-circle goniometer equipped with a rotating anode generator (Cu Kα, λ=1.5418 Å). We selected the (200) reflection to be recorded since it corresponds to the substrate orientation, and it was therefore rather easy to adjust it in the diffraction position. This reflection will give us informations on the interreticular spacing perpendicularly to the layer's plan. The recorded diffraction pattern (Fig. 5) shows two (200) reflections, one from the layer and one from the substrate ($2\theta_{200}$ = 6.882°). The reflection corresponding to the layer appears at a lower angle than expected from single crystal (unstressed) structures of the same composition ($2\theta_{200}$ = 6.855° instead of

6.87°). This is most probably due to a tetragonal distortion of the crystallographic cell in the epitaxial layer. The cell parameters are reduced in the substrate's plan ($\vec{b}$ and $\vec{c}$) to compensate the mismatch, leading to an increase of the cell parameter perpendicularly to the substrate ($\vec{a}$ is increased from 25.7316 Å to 25.7902 Å). Consequently, the epitaxial layer is under important stress which is present throughout the layer (in spite of its thickness) and is released at the surface by a series of linear distortions running parallel to the $\vec{c}$ crystallographic axis (lines visible on Fig. 4). These distortions of the layer's surface show that it is necessary to reduce the cell parameters mismatch to realize layers of suitable quality for wave-guide structures.

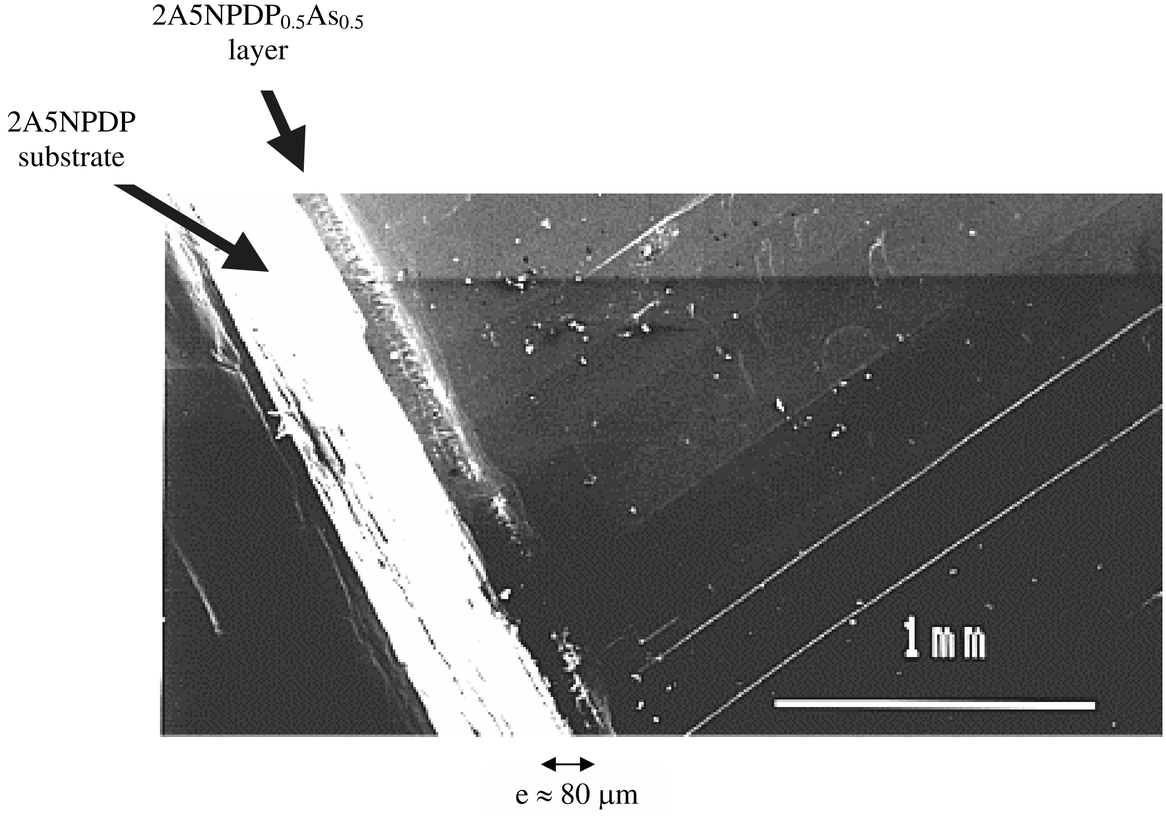


Fig. 4. Scanning electron microscopy image, side view showing both the $2A5NPDP_{0.5}As_{0.5}$ layer and the (100) 2A5NPDP substrate.

The most straightforward method to reduce the mismatch is to deposit layers with a composition closer to that of the substrate. Thus, we deposited $2A5NPDP_{0.8}As_{0.2}$ layers on 2A5NPDP substrates. Another way to reduce the cell parameters mismatch is to use substrates of different substrate orientations, in our case, we selected (010) crystal plates in addition to the (100) ones. Changing the orientation of the substrate not only modifies the cell parameter mismatch but also affect many other parameters such as the growth rate of the layer or the growth mechanisms. The thickness of the resulting epitaxial layer depends on the growth rate of the layer and on the time the substrate is left in the solution. In order to determine the average growth rates for each orientation and for different supersaturations, the substrates were partially masked and kept in the solution for a precise period of time. The growth rate for each substrate could be then determined by measuring the thickness of the layer between the masked and unmasked portion of the substrate. This procedure was used for two relative supersaturations $\sigma = 1.5\%$ and 6%. In order to have the average growth rates along the three crystallographic axes, (001) crystal plates of 2A5NPDP were used in addition to the two substrate orientations previously selected. These growth rates for the two relative supersaturations are the following:

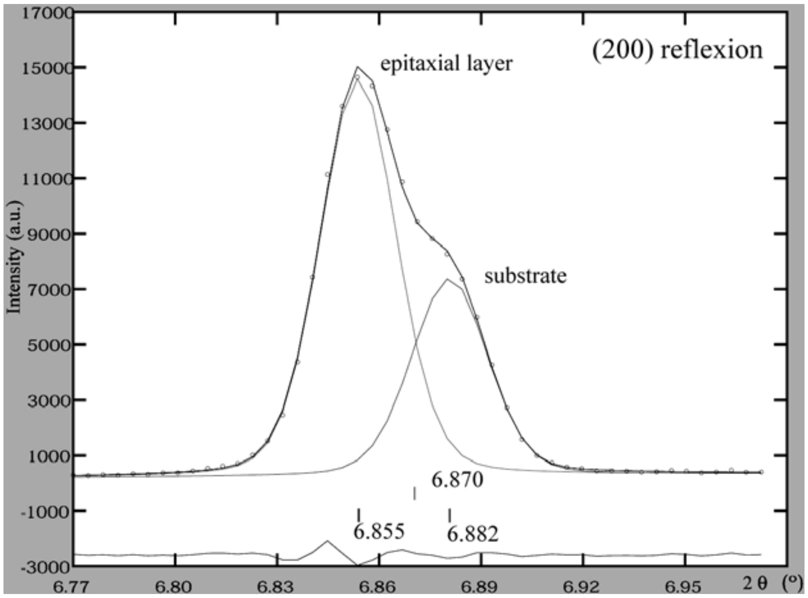
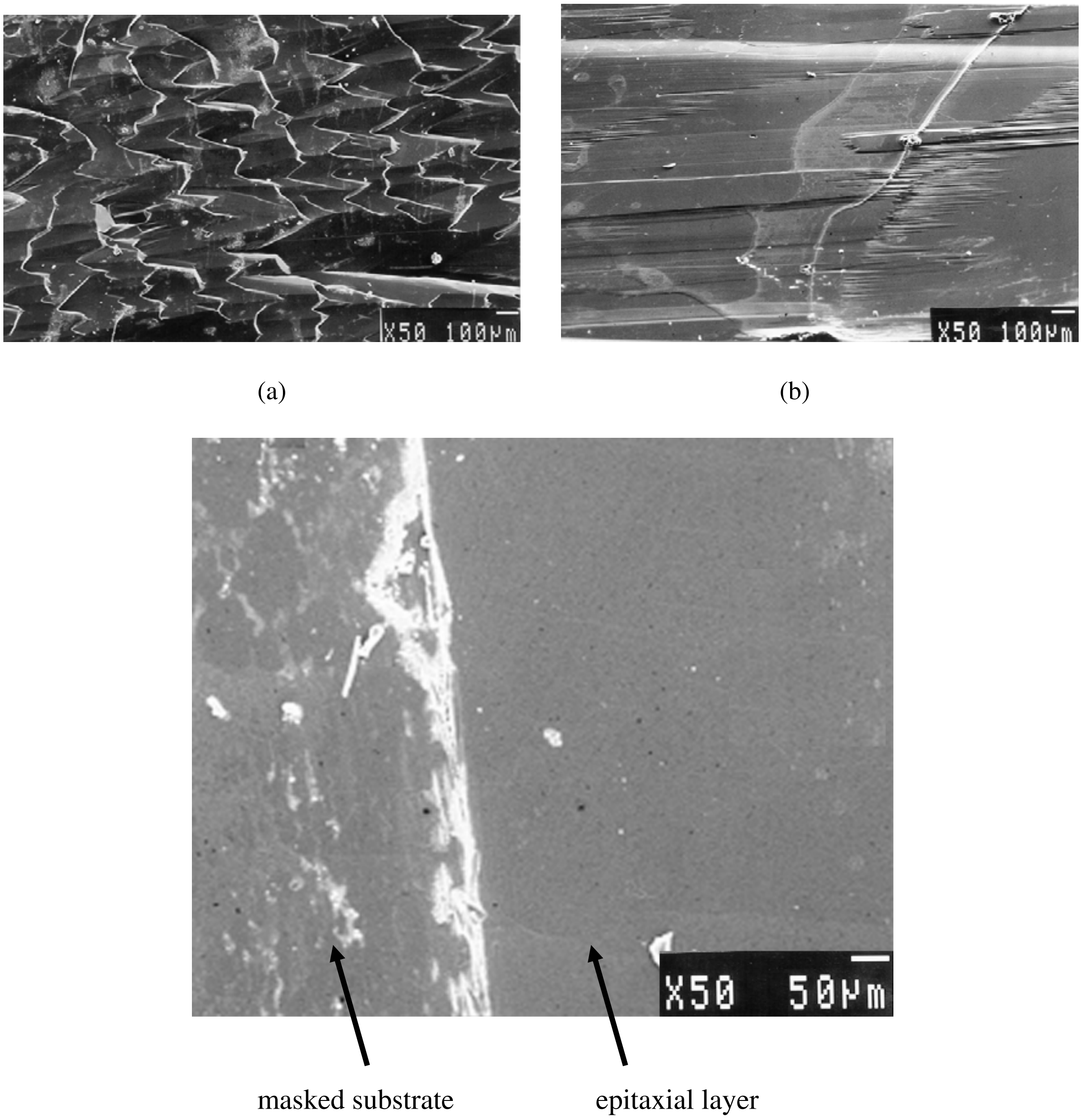


Fig. 5. X-ray diffraction pattern, (200) reflections of a 2A5NPDP$_{0.5}$As$_{0.5}$ layer (6.855°) and 2A5NPDP substrate (6.882°), the expected position of the (200) reflection for the 2A5NPDP$_{0.5}$As$_{0.5}$ is also shown (6.870°).

$$\sigma = 1.5\% : \quad R_{\vec{a}} = 1\ \mu\text{m/h}, \quad R_{\vec{b}} = 6 \pm 2\ \mu\text{m/h}, \quad R_{\vec{c}} = 31 \pm 7\ \mu\text{m/h}$$

$$\sigma = 6\% : \quad R_{\vec{a}} = 9 \pm 3\ \mu\text{m/h}, \quad R_{\vec{b}} = 40 \pm 6\ \mu\text{m/h}, \quad R_{\vec{c}} = 65 \pm 5\ \mu\text{m/h}$$

These values clearly show the growth anisotropy of this hybrid solid solution along the three crystallographic axes. The growth is favored along the c-axis resulting in stick shaped crystals. The orientation of the substrate also influences the growth mechanism of the layer leading to different surface morphology evidenced by scanning electron microscopy. On (010) substrates, the layer grows by two-dimensional nucleation leading to the development of islands on the surface. These islands present flat faces of identical orientation giving a general facetting of the epitaxial layer (Fig. 6a). On the other hand, no facetting is observed for (100) substrates. In this case, the layer grows by two-dimensional nucleation and advancement of steps parallel to the $\vec{c}$ direction. For high values of supersaturation (σ = 6%), steps nucleate before the completion of the previous layer leading to a rough surface structure (Fig. 6b). For lower values of supersaturation (σ = 1.5%), each layer is completed before new steps nucleate leading to a flat surface (Fig. 6c).



(a) (b)

(c)

Fig. 6. 2A5NPDP$_{0.8}$As$_{0.2}$ epitaxial layer grown on 2A5NPDP substrates orientations (a) Facetting of the layer on a (010) substrate; (b) layer grown at a relative supersaturation of $\sigma = 6\%$ on a (100) substrate; (c) layer grown at a relative supersaturation of $\sigma = 1.5\%$ on a (100) substrate, the left part is the masked substrate and the right side is the epitaxial layer.

4. Discussion

4.1 2A5NPDP$_{(1-x)}$As$_x$ single crystals

We have demonstrated that large single crystals of very high quality and chemically homogeneous can be grown in solution for all the compositions of the solid solution 2A5NPDP$_{(1-x)}$As$_x$ ($0 \leq x \leq 1$). Moreover, the first attempts of rapid growth [16] showed that such technique can be applied to hybrid crystals allowing an increase of the growth rates of about one order of magnitude: from 1mm/day to 1cm/day. These results would be very important for an eventual industrial application of a crystal of this family. In addition, all these hybrid crystals display bulky morphologies and their convenient stability (chemical, thermal and mechanical hardness) allows easy slicing and polishing to prepare optical devices. These characterizations were carried out for different compositions of the solid solution. This demonstrated that linear and nonlinear optical properties could be adjusted by changing the As/P ratio in the inorganic sub-network [17]. For instance, it has been shown that the three principal refractive indices increase as a function of the arsenate amount in the mineral sub-network: an increase of about 0.5 10^{-3} can be obtained by increasing the As content by 30%. Such tuning of the properties is impossible for organic molecular crystals since there is no solid solution. The maximum change of refractive indices between two composition of the $2A5NPDP_{(1-x)}As_x$ solid solution is about 1.5×10^{-3}. This is enough to realize of wave-guide structures.

4.2 Epitaxial layers

In order to realize wave-guide structures with a difference in refractive indices as large as possible we have deposited layers of different compositions on 2A5NPDP subtrates. We showed that layers of compositions differing widely from the substrate could be deposited with success in spite of a significant cell parameter mismatch. The maximum difference in composition tested is the $2A5NPDP_{0.5}As_{0.5}$/2A5NPDP system. This growth epitaxy is favored by the great plasticity of the hybrid organic-inorganic structure. Indeed, the $2A5NPDP_{0.5}As_{0.5}$ layer is submitted to an important stress due to a high tetragonal distortion evidenced by X-ray diffraction (Fig. 5). The associated constraints relax at the surface leading to distortions. They also make the layer more fragile, upon moderated pressure perpendicularly to the layer, it can separate from the substrates surface along the (100) cleavage plan. In order to reduce the cell parameters mismatch, another orientation of the 2A5NPDP substrate was tested. Thus, different growth mechanisms were observed between substrates with (100) and (010) orientations. This difference of growth mechanism is directly related to different types of crystal faces in the PBC theory [18,19]. Indeed, the growth of the (010) faces is unstable (K type, kinked) while that of the (100) face is stable (F type, Flat) as can be see on Figs. 2a and 2c. The substrates with a (010) orientation (K type) favor the Volmer-Weber mechanism of growth [20], the deposited molecules form islands on the surface, Fig. 2a. When these islands grow, other stable faces appear on each one of them resulting in the general facetting of the layer. This growth mechanism is not very favorable for the realization of wave-guide structures. Not only because of the roughness of the layers surface but also because the growth of independent islands leads to a higher mosaicity and defects at the joints of islands. On the other hand, substrates with a (100) orientation are F type and favor Frank-Van de Merwe (layer-by-layer) growth mechanism [20]. In this case, a step formed by a screw dislocation emerging at the surface or by two-dimensional nucleation will advance and uniformly cover the whole substrate's surface. If the supersaturation is too high, nucleation may occur before the previous layer is completed. By reducing the relative supersaturation to $\sigma = 1.5\%$ we were able to obtain layers with a flat surface. This demonstrate the possibility to realize, with hybrid organic-inorganic solid solutions, structures presenting all the features of wave-guides: significant refractive indices difference between the layer and the substrate and sharp and flat air - epitaxial layer - substrate interfaces. In order to realize wave-guide structures with 2A5NPDP substrates, the choice of the deposited composition has to be optimized to obtain convenient indice difference between the layer and the substrate with the lower cell parameter difference. Moreover, the growth conditions have to be refined to obtain thinner layers in order to reduce the number of propagation modes in the guide. The optical characterizations of these wave-guides are under investigation.

5. Conclusion

The hybrid organic-inorganic crystals represent an interesting compromise for nonlinear optical applications in the visible and near IR regions. Their quadratic nonlinear efficiency is comparable or higher to those of the inorganic crystals which are industrialized ($KTiOPO_4$, β-Ba_2BO_4...), with improved stability compared to that of organic molecular crystals. Other advantages of these hybrid compounds are to present bulky morphologies and to obtain large crystals of high quality by standard methods such as the temperature lowering one. The existence of solid solutions and the resulting possibility to realize wave-guide structures is another asset of these hybrid phases that has been detailed more specifically in this work. Of course, the compromise that is proposed by this first hybrid family is not perfect. For instance, their stability remains too limited, (decompositions around 200°C), to allow an extensive use of these H-bond salts as active medium in optical devices without a protecting cell. For theses reasons other hybrid organic-inorganic family are currently under investigation. In order to improve the overall stability, the chromophore has to be anchored on the inorganic sub-network through iono-covalent bonds instead of H-bonds.

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