Journal of Crystal Growth 56 (1982) 141–150
North-Holland Publishing Company

A COMPARISON BETWEEN GEL GROWN AND SOLUTION GROWN CRYSTALS – CASE OF ADP AND KDP *

F. LEFAUCHEUX, M.C. ROBERT and E. MANGHI **

Laboratoire de Minéralogie–Cristallographie, Tour 16, 4 Place Jussieu, F-75230 Paris Cedex 05, France

Received 4 June 1981

Water soluble crystals such as ADP and KDP have been grown in TMS gels by different techniques. A study of growth defects by X-ray topography shows that these gel grown crystals obtained by a very simple technique can be compared to crystals grown from solutions using elaborated systems.

1. Introduction

The gel growth techniques have mainly been developed for materials which are difficult to obtain by other techniques, for example insoluble materials. Very few studies [1–3] are devoted to gel growth of water soluble crystals which can be easily grown by classical solution growth techniques.

In this study, the growth defects in gel grown ADP and KDP crystals are presented and compared with those observed in similar solution grown crystals [4–14].

2. Experimental

The medium used for the growth is obtained from tetramethoxysilane (TMS) which allows to obtain gelled saturated solutions of ADP or KDP when TMS is mixed with the solution. Low concentrations of TMS (2 to 10 vol%) have been used. During the gelling process, the temperature is kept constant a few degrees above the saturation temperature (45°C) in order to prevent the formation of parasitic nucleation. Then the test tubes are set in a growth bath. Three methods allow to get a supersaturated medium:

(i) the bath temperature is slowly decreased as usually in solution (T);
(ii) a liquid in which the material is slightly soluble, is left to diffuse through the gel column at constant temperature (D);
(iii) these both techniques are used simultaneously in order to increase the growth rate (D + T).

The iron content in the saturated solution was 20 μg per g of KDP or 10 μg per g of ADP. The pH of the saturated solution at 45°C is 4.50 for KDP and 4.10 for ADP solutions. Alcohol (KDP) and acetone (ADP) are used for the diffusion techniques.

3. Optical observations

Fig. 1 presents KDP crystals grown in a 2% TMS gel. The crystals grown by the first technique (T; fig. 1a) are few but large and optically clear. In the third technique (D + T; fig. 1b), more crystals are formed along the gel column but those grown near the interface often present macroscopic inclusions or cracks, only crystals grown in the middle part of the tube are optically clear and were studied for characterization.

KDP and ADP crystals are tetragonal, space groupe $I\bar{4}2d$. They display the same habit with prismatic {100} and pyramidal {101} faces. Usually (fig. 1a), they are elongated along the *c*-axis. But, plate like crystals extended parallel to a prismatic face can be found (see fig. 3).

* Paper presented at ICCG6, Moscow, 1980.
** Permanent address: Division Fisica del Solido, CNEA, Avenida Libertador 8250, 1429 Buenos Aires, Argentina.

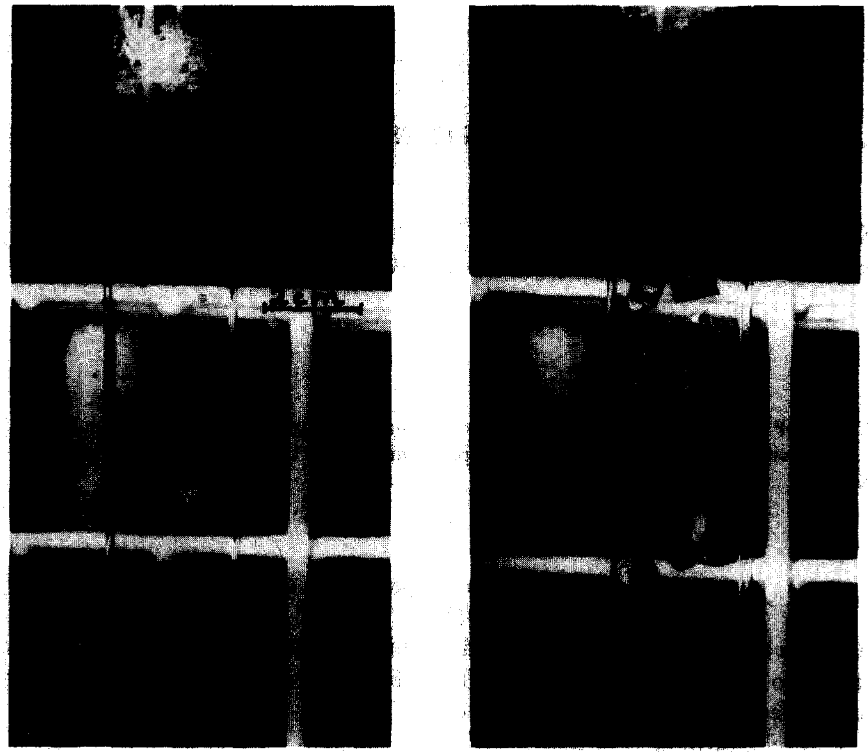

Fig. 1. KDP crystals grown by T (a) and D + T (b) techniques.

As grown crystals and (001) slices have been characterized by X-ray topography (Lang method).

4. X-ray characterization: main features

The defects observed on Lang topographs of gel grown crystals, are mainly dislocations, inclusions and strain at growth sector boundaries. Fig. 2a shows a topograph of a (001) slice cut out of an ADP crystal and the corresponding growth sector distribution is reported on fig. 2b. The unequal developments of pyramidal sectors are related to differences in their growth rates: the (011) sector has grown slower than the neighbouring pyramidal sectors. In such a case, boundaries (S_2) appear between the slow growing pyramidal sector and the adjacent prismatic sectors. The boundaries (S_1) between prismatic and pyramidal sectors are visible as faint contrasts but only for the parts lying parallel to the reflector plane; on the contrary, the part (S_1') becomes visible with a 200 reflection, suggesting in each case a fault vector normal to the limit. Only three growth dislocations (d) are present in the prismatic sectors. The main defects in this slice are two large inclusions (I) located in the pyramidal part. Some dislocation loops (l) surrounding these inclusions, do not propagate far from them, so the perturbated region is limited and the quality of the slice is rather good. This crystal was grown in a 5% TMS gel and as previously shown [15], the number and the size of the inclusions and consequently the dislocation density can strongly decrease by lowering the gel density or by varying the growth conditions.

In some cases, very few defects are present in gel grown crystals as shown on fig. 3; this as grown ADP crystal presents only one main defect, a dislocation line (d). Indeed if the surface defects (p) are excepted, the faint contrasts are related to strained growth sector boundaries (S); two inclusion lines (I)

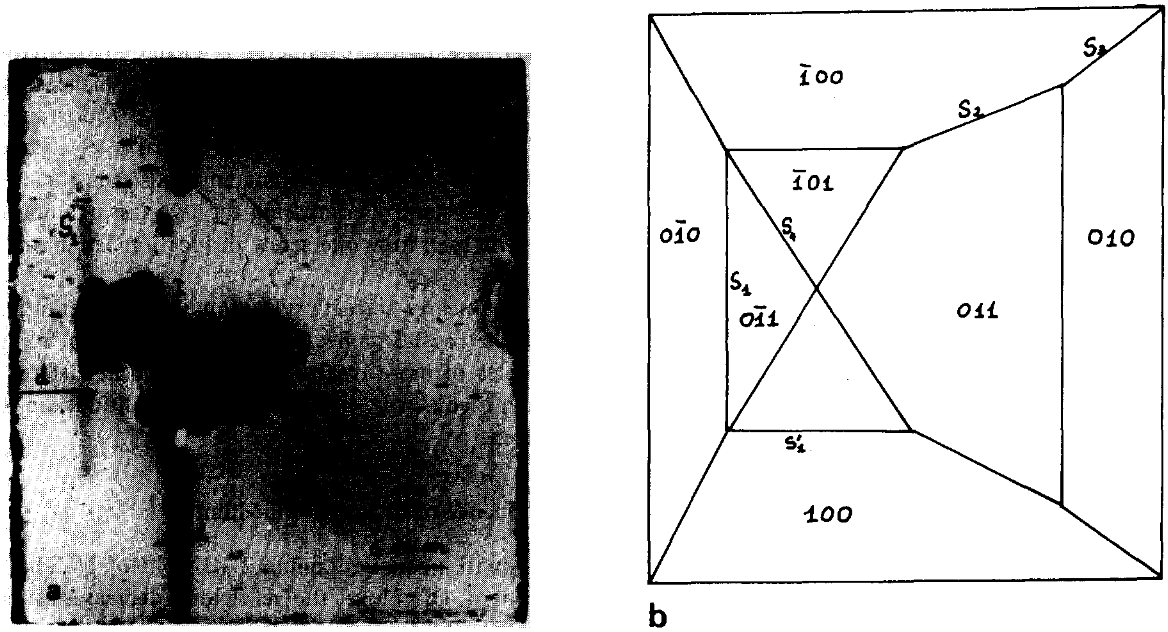

Fig. 2. (a) Topograph of a (001) plate cut out of an ADP crystal grown in a 5% TMS gel by the D + T technique. Growth duration: 2 months; AgKα Ref. 020. (b) Sector distribution in the crystal.

reveal local perturbations; furthermore, fine fringes (f) due to the wedge shaped pyramidal sectors confirm the good quality of this crystal. So let us discuss about this unique dislocation: it is out of contrast for 022 and 0$\bar{2}$2 reflections, therefore it corresponds to a pure screw dislocation. This dislocation has increased the growth rates of the two opposite sectors in which it propagates: from thickness measurements, it can be

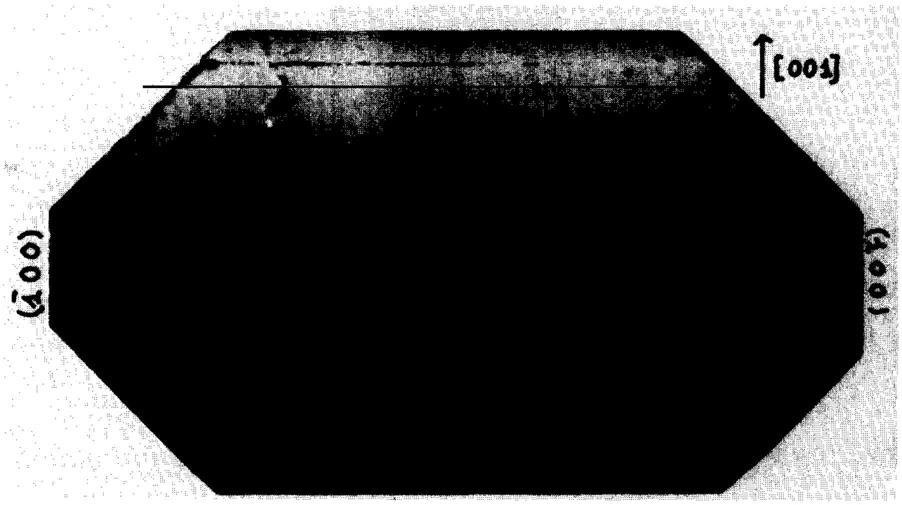

Fig. 3. Topograph of an as grown crystal of ADP obtained in 4 days by the D technique, in a 5% TMS gel. AgKα Ref. 200; thickness: 0.9 mm; μt = 0.26.

deduced that the growth rates of (100) and ($\bar{1}$00) sectors is ten times higher than those of the other prismatic (010) and (0$\bar{1}$0) sectors. It results a platelet shape for this crystal.

Fig. 4 corresponds to a remarkable ADP crystal: no dislocations are visible in the whole crystal, only faint black and white contrasts (S) are detected at the boundaries between prismatic and pyramidal sectors. These contrasts become reversed if the sign of g is changed; as previously shown by Fishman [16], this defect corresponds to a lattice parameter difference whose sign is determined from the g-direction in the case of anomalous transmission [10]. Thus, for this crystal, the lattice parameter is higher in prismatic sectors than in pyramidal sectors. Precise measurements with a technique of plane wave topography [17] are now in progress. This crystal is elongated along the c-axis and not along an a-axis as in the precedent case: so by comparing the two last examples, it can be seen how one screw dislocation can modify the morphology.

These nearly perfect crystals are not representative of all the crystals collected in gel experiments. Some examples of more typical crystals grown in different growth media or in different growth conditions are to be given.

Fig. 4. Topograph of an as grown crystal of ADP obtained in a 2% TMS gel by the D + T technique. Growth duration: 1 month; MoKα Ref. 200; thickness: 2.75 mm; μt = 1.5.

5. Influence of the growth medium

Growth media containing 2–10 vol% of TMS have been used. Of course, the gel rigidity decreases as the TMS content decreases. Furthermore, the gelling process being a polymerization process is greatly dependent on the temperature, so the gel rigidity is reduced

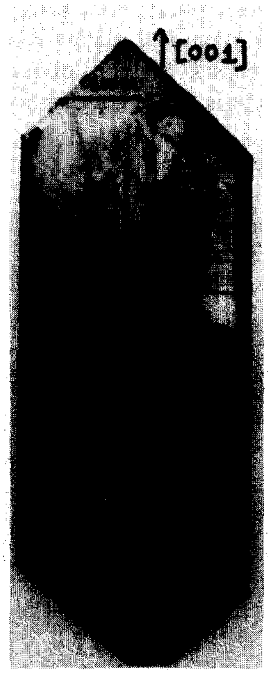

Fig. 5. Topograph of an as grown crystal of KDP obtained in a 10% TMS gel by the T technique. Growth duration: 15 days; MoKα Ref. 200; thickness: 2 mm; μt = 3.2.

by lowering the temperature. The main defects in gel grown crystals remain the formation of gel inclusions especially at the beginning of the growth. As discussed by Henish [18], the incorporation of gel particles is avoided if the gel is removed far from the growth interface. This gel rejection occurs easily, when the crystal is large enough and interconnected gel cusps [3,19] are formed but it is more difficult at the nucleation step especially as the gel is rigid.

This is clearly seen on KDP crystals grown in 10% TMS gel (fig. 5). The central part is strongly contaminated and bundles of dislocations start from these gel inclusions. The crystals grown in a 5% TMS gel by the same T-technique contain only small inclusions which are not sources of dislocations as shown on fig. 6. All the dislocations (d) start from the nucleus (N) and propagate mainly in the prismatic sectors. Some of them remain trapped at the boundaries between prismatic and pyramidal sectors (S). This crystal exhibits clearly an unequal development of the different pyramidal faces. The crystals grown in a 2% TMS gel present about the same features as for the precedent case. Of course, the number of dislocations generated at the beginning decreases as the gel density decreases. But a strong limitation for the use of low concentration gels is to be considered: the medium does not maintain any longer the crystal at the nucleation site as the growth and consequently the weight progress, the gell fissures and the crystal gradually falls down.

Fig. 6. Topograph of an as grown crystal of KDP obtained in a 5% TMS gel by the T technique. Growth duration: 15 days; MoKα Ref. 200; thickness: 1 mm; μt = 1.6.

6. Influence of growth conditions

Figs. 7 and 8 display topographs of crystals grown in a 5% TMS gel as in the precedent case (fig. 6); the difference concerns the use of diffusion processes either at constant temperature (fig. 7) or with a temperature decrease (fig. 8). The crystals grown by the three methods are rather similar concerning the distribution of the dislocations. Those dislocations are generated at the beginning of the growth and propagate normal to each growth front. They are easily trapped at growth sector boundaries. All the crystals grown by diffusion present thick fringes F, which are not growth bands: section topographs indicate that they correspond to faults between growth sectors which are seen superimposed in the translation topographs (fig. 7b presents the sector distribution visible on fig. 7a). These fringes show a faint contrast if they correspond to adjacent growth sectors of the same type: pyramidal (F_4) or prismatic (F_3). This contrast is marked if the fault concerns growth sectors of different types (F_1, F_2) (see also fig. 8). These faults are clearly seen on (001) slices cut out of such crystals (fig. 9). Fringes (F_1, F_2) are observed between prismatic and pyramidal sectors (S_1 or S_2) as only very faint contrasts are detected between two pyramidal sectors (S_4) or two prismatic sectors (S_3). Furthermore, these faults must be related to the diffusion of alcohol: as seen clearly on fig. 8, fringes do not occur all along the growth but only at the beginning; in fact, after some weeks, the alcohol content must be considered as constant and the supersaturation is then created by the temperature decrease as for the crystal fig. 6 which does not present such fringes.

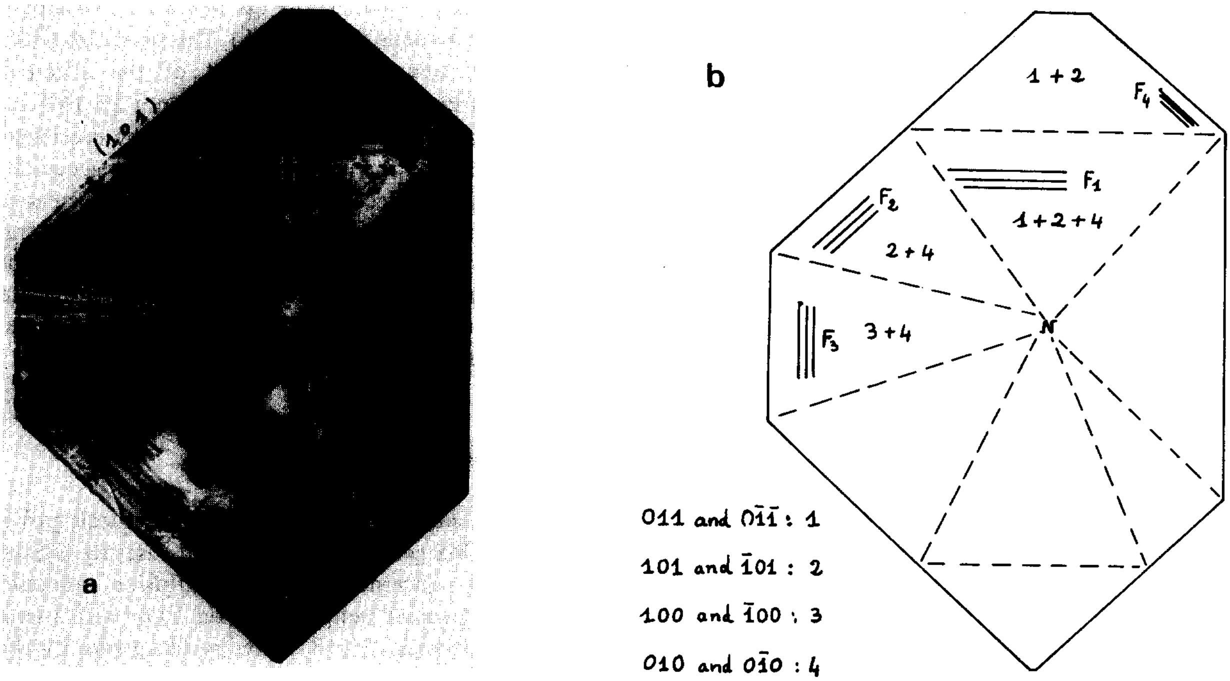

Fig. 7. (a) Topograph of an as grown crystal of KDP obtained in a 5% TMS gel by the D technique. Growth duration: 15 days; MoKα Ref. 200; thickness: 3.25 mm, μt = 5.3. (b) Sector distribution in this crystal.

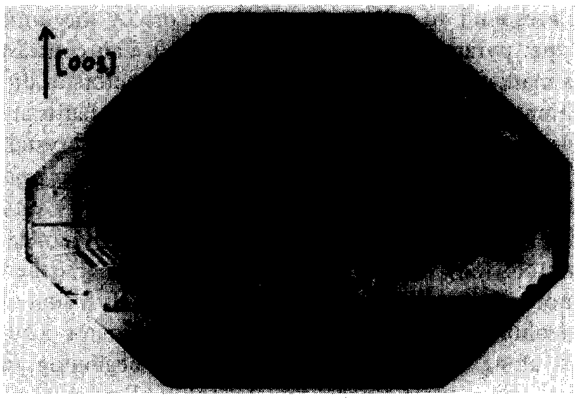

Fig. 8. Topograph of an as grown crystal of KDP obtained in a 5% gel by the D + T technique. Growth duration: 60 days; AgKα Ref 200; thickness: 3.9 mm; μt = 1.2

7. Comparison between gel and solution grown crystals

7.1. Growth conditions

KDP and ADP solution grown crystals have been characterized by many authors. First, surface studies and kinetic measurements of growing crystals [20–22] have allowed to propose a growth mechanism for the two types of faces {100} and {101} in presence of various impurities. Furthermore, X-ray topographic studies have well established the crystalline quality of ADP and KDP grown in different conditions as seen on table 1. The crystals grown from solutions are obtained in a forced convection regime. In order to prevent instabilities, the growth parameters have been controlled: elaborated stirring systems, slow cooling rates and a careful temperature stabilization allowed to optimize the growth conditions. On the contrary, the gel grown crystals being obtained mainly in a diffusion regime, high cooling rates and a

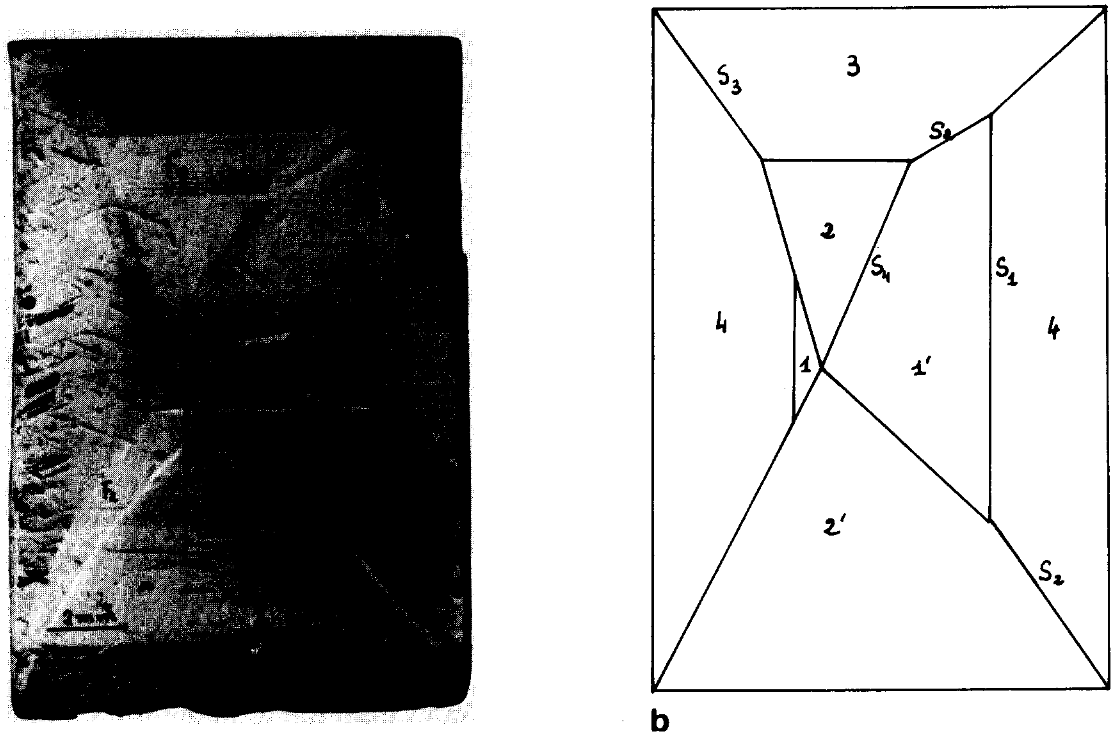

Fig. 9. (a) Topograph of a (001) slice cut of a KDP crystal grown in a 5% TMS gel by the D technique. MoKα Ref. 020; $\mu t = 1.6$. (b) Sector distribution in this slice. For the notations see fig. 7b. The irregular shape of pyramidal sectors indicate different growth rates (R) of corresponding faces $R_1 > R_2 > R_{1'} > R_{2'}$.

rough temperature stabilization have been applied.

The growth rates are of the same order of magnitude for solution and gel grown crystals. So the mass transfer at the interface must be about the same in both cases. As high concentration gradients are needed to realize this transfer only by diffusion, the "supersaturation" varies in the gel from one point to another: near the growing interface, it is about the same as in solution but far from the interface, the values of the supersaturation must be much higher in gels than in solutions. Nevertheless, few nuclei appear in the gel, this fact confirms that the nucleation should occur at higher supersaturation in gel than in solution systems [23].

7.2. *Morphology of the crystals*

An important growth defect in solution grown KDP and ADP crystals concerns the development of high-index faces instead of normal prismatic faces. The deviation angle (tapering angle) α is a measure for the incorporation of impurities (such as iron, chromium) in the prismatic sectors [9,11]. Tapering was not observed in gel even for samples grown with high iron content (up to 90 ppm). The absence of tapering in gel grown crystals cannot be explained from the results of solution growth studies; indeed, the use of temperature decrease [14], unstirred and impure solutions [9–12] would lead to a strong tapering.

7.3. *Lattice defects*

7.3.1. *Growth bands*

Growth bands are always present in ADP and KDP solution grown crystals; they are essentially located in prismatic sectors but a few of them can be detected in pyramidal ones. Belouet et al. [10,11] have related the importance of growth bands to the impur-

Table 1

Literature	Growth method and Crystal	Crystallization temperature, $T_c \pm \Delta T_c$	Supersaturation, σ	pH	Impurity (μg/g of material) in the mother solution (Fe)	Growth rate $R_{(101)}$ (10^{-6} cm/s)
Lutsau et al. [7], Klapper et al. [8]	ADP and KDP on seeds in a stirred solution by temperature decrease (a)	–	Not given	Not given	–	–
Belouet et al. [9–12]	KDP on (001) seeds in a stirred solution (a)	$28 < T_c < 55°C$ $\Delta T_c = 0.01°C$	2–6%	4–6	1.7–30	1
Chernov et al. [13]	ADP on a seed in a solution flux at constant temperature (b)	–	0.5–1%	4.4	–	0.2
Dam and Van Enckevort [14]	KDP on (001) seeds by the two methods (a) and (b)	(a) 0.15°C/day (b) $T_c = 29.50°C$	(b) 4.2%	–	10	1
Our gel experiments	ADP and KDP crystals spontaneously nucleated by (a) and (b)	(a) 0.4°C/day (b) $T_c \simeq 40°C$	Unknown	4.1 (ADP) 4.5 (KDP)	10 (ADP) 20 (KDP)	0.4

ity content. For instance, growth bands in pyramidal sectors are avoided only for very low impurity concentrations (Fe ~ 1.7 ppm). Gel grown crystals are usually obtained with an iron content of 20 ppm, nevertheless no growth bands are detected (figs. 2 and 9) even by using a more sensitive technique (plane wave topography).

7.3.2. Growth sector boundaries

In solution grown crystals, the boundaries between prismatic and pyramidal sectors are always visible; for low impurity contents, the boundaries between pyramidal sectors become nearly invisible [10]. The contrasts at the boundaries are related to lattice differences between neighbouring sectors. Gel grown crystals (figs. 2 and 9) present only faint contrasts at the boundaries between prismatic and pyramidal sectors; in some cases, no contrasts are visible between sectors of the same type.

7.3.3. Dislocations

The dislocation density is very low in gel grown crystals as compared to solution grown crystals [10]. This very low density can be due first to the growth mode which takes place in gel namely by diffusion, but also to the high supersaturation corresponding to the nucleation step: in fact the small value of the specific surface free energy of ADP [13] can lead to a bidimensional nucleation and ADP crystals without any dislocation (fig. 4) can easily be obtained in gel. Dislocation directions in solution grown KDP have been calculated in relation to their Burgers vectors [8]. Some of them, calculated for the prismatic sector of not tapered crystals could not be observed in the crystals obtained by Fishman, these crystals being strongly tapered. It is not the case in gel grown crystals, the observed directions really correspond to the calculated ones in absence of tapering. The refraction of dislocation lines from one sector to another is generally dependent on the relative growth rates of these neighbouring sectors. Some dislocations remain trapped in the boundary (figs. 3, 6, 8) and as mentionned by Chernov in the case of ADP [13], they can determine the orientation of the boundary (case of the last dislocation leaving the pyramidal sector). In our gel grown crystals, two types of boundary directions are found. First, the limit is oriented nearly normal to the pyramidal sector (d_1 in fig. 6), then, the pyramidal growth rate was high and the crystal displays the usual habit. Secondly, the limit (fig. 8) takes the orientation of the d_2 dislocation (fig. 6) which corresponds to a calculated direction in a prismatic sector. In that case, the growth rate of the prismatic sector was high and the crystal is elongated along the *a*-axis.

8. Conclusion

The present study gives an example of comparisons between crystals grown from free and gelled solutions. It has been shown that growth defects such as growth bands, dislocations are suppressed or reduced by gelling the growth medium. Nearly perfect crystals can nucleate and grow in such systems. These results must strengthen the interest which has recently been observed concerning the gel growth techniques.

References

[1] D.A. Glocker and J.F. Soest, J. Chem. Phys. 51 (1969) 3143.
[2] B. Brezina and M. Havrankova, Mater. Res. Bull. 6 (1971) 537.
[3] M.S. Joshi and A.V. Antony, J. Mater. Sci. 13 (1978) 939.
[4] R.F. Belt, J. Appl. Phys. 35 (1964) 3063.
[5] R.D. Deslattes, J.L. Torgesen, P. Paretzkin and A.T. Horton, J. Appl. Phys. 37 (1966) 541.
[6] M. Yoshimatsu, Japan. J. Appl. Phys. 5 (1966) 29.
[7] V.G. Lutsau, Ju.M. Fishman and I.S. Res, Kristall Tech. 5 (1970) 445.
[8] H. Klapper, Ju.M. Fishman and V.G. Lutsau, Phys. Status Solidi (a) 21 (1974) 115.
[9] C. Belouet, Acta Electron. 16 (1973) 340.
[10] C. Belouet, E. Dunia and J.F. Petroff, J. Crystal Growth 23 (1974) 243.
[11] C. Belouet, M. Monnier and J.C. Verplanke, J. Crystal Growth 29 (1975) 109.
[12] C. Belouet and W.T. Stacy, J. Crystal Growth 44 (1978) 315.
[13] A.A. Chernov, I.L. Smol'skii, V.F. Parvov, Yu.G. Kuznetsov and V.N. Rozhanskii, Dokl. Akad. Nauk SSSR 248 (1979) 356.
[14] B. Dam and W.J.P. van Enckevort, J. Crystal Growth 51 (1981) 607.
[15] F. Lefaucheux, M.C. Robert, E. Manghi and H. Arend, J. Crystal Growth 51 (1981) 551.
[16] Ju.M. Fishman and V.G. Lutsau, Phys. Status Solidi (a) 3 (1970) 829.

[17] M.C. Robert, F. Lefaucheux, M. Sauvage and M. Ribet, J. Crystal Growth 52 (1981) 976.
[18] H.K. Henish, Crystal Growth in Gels (Pennsylvania Univ. Press, 1968).
[19] J. Hanoka, J. Appl. Phys. 40 (1969) 2694.
[20] J.L. Torgesen and R.W. Jackson, Science 148 (1965) 3672.
[21] R.J. Davey and J.W. Mullin, J. Crystal Growth 23 (1974) 89.
[22] R.J. Davey and J.W. Mullin, J. Crystal Growth 26 (1974) 45; 29 (1975) 45.
[23] G.M. van Rosmalen, W.C.J. Marchee and P. Bennema, J. Crystal Growth 35 (1976) 176.
[24] E. Dunia, Thesis, University of Paris VI (1980).