

THE INFLUENCE OF MANGANESE IONS AS IMPURITY ON THE HABIT  
OF ADP CRYSTALS

Z. Juranić, M.Lj. Napijalo, B. Žižić, R. Ristić  
The Faculty of Natural Sciences and the Institute  
of Physics, Belgrade

The natural habit of ADP crystal is a combination of a tetragonal prism and two tetragonal pyramids, Fig.1. The aim of this work was to investigate the influence of manganese ions  $Mn^{2+}$ ,  $Mn^{3+}$ , and  $MnO_4^-$  on the habit of ADP crystal depending on the supersaturation ( $\sigma$ ) of the solution.

$Mn(CH_3COO)_2 \cdot H_2O$ ,  $MnCl \cdot 4H_2O$  and  $NH_4MnO_4$  were added to the ADP appropriately supersaturated aqueous solution, as impurity  $NH_4MnO_4$  was obtained by the reaction of  $KMnO_4$  with  $NH_4NO_3$  and by recrystallization. The stoichiometric concentration of  $Mn^{3+}$  was  $1.3 \cdot 10^{-3}$  mol/l for pH=3.6. The growth of crystal seeds ( $0.5 \times 1 \times 0.5$  mm<sup>3</sup>) occurred in two ways: in the Holden type crystallizer with temperature gradient of  $-0.1^\circ C/24$  h, and in the crystallization cell in which both, the temperature (T) and supersaturation ( $\sigma$ ) were maintained constant.

The influence of  $Mn^{2+}$  as the impurity ( $C_1 = 1.3 \cdot 10^{-3}$  mol/l) on the crystal habit was not observed, and the spectroscopic analysis of these crystals has shown negligible presence of  $Mn^{2+}$  ions in them (about 1 ppm). The influence of  $MnO_4^-$  ions as the impurity on the crystal habit ( $C_2 = 4 \cdot 10^{-3}$  mol/l) was not noticed. The stoichiometric mixture of  $Mn^{2+}$  and  $MnO_4^-$  is such that it gives the concentration of  $1.3 \cdot 10^{-3}$  mol/l of  $Mn^{3+}$  ion causing the change of habit of ADP crystal, which depends on the supersaturation of the solution ( $\sigma$ ) as it is shown in the table 1 and in Figs. 2 and 3.

At the supersaturation  $\sigma < 0.082$  the tapering of the prismatic crystal faces occurs. This phenomenon has

been found previously (1,2,3) in case of impurities  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Al}^{3+}$  ions also.

Table 1.

| $\sigma = \frac{c-c_0}{c_0}$ | $R 010  \cdot (10^{-7} \text{ ms}^{-1})$ |                          | The remarks  |
|------------------------------|--|--------------------------|--|
|                              | with $\text{Mn}^{3+}$                    | without $\text{Mn}^{3+}$ |  |
| <0.08                        | not defined                              | 0.23                     | not defined and rough crystal faces                              |
| 0.082                        | <0.02                                    | 0.28                     | appearance of new faces  |
| 0.087                        | <0.02                                    | 0.60                     | appearance of new faces  |
| 0.093                        | <0.05                                    | 0.63                     | regular ADP cristal with the dark yellow coloured prismatic part |
| 0.097                        | <0.12                                    | 0.68                     | - " -  |

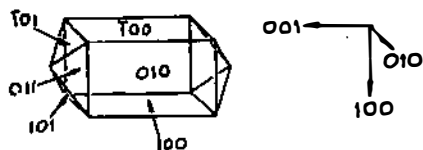


Fig. 1.



Fig. 2.



Fig. 3.

In the supersaturation range from 0.082 to 0.087 the new crystal faces appear: four tetragonal and four triangular faces at the corner between the prismatic and the pyramidal faces of the crystal (Fig.2). The appearance of the new crystal faces is caused by complex adsorption of  $Mn^{3+}$  on prismatic and pyramidal crystal faces<sup>(4)</sup>.

At supersaturation  $\sigma > 0.093$ , the growth of prismatic crystal faces is slowed down (Table 1). That phenomenon as well as the yellow-brown coloured phenomena inside the prismatic part of the crystal (Fig. 3) suggest that in the given range of supersaturation the adsorption of  $Mn^{3+}$  ingradient occurs on the prismatic crystal faces.

#### References:

1. I.M.Biteva; "Rost kristalov", 5 (1963), 219 (in russian)
2. J.W.Mullin, A.A.Amatoviodhana; J.Appl.Chem, 20 (1970)
3. R.J.Davey, J.W.Mullin; J.Crystal Growth, 26 (1974) 45
4. P.Hartman, ed. Crystal Growth an Introduction (1973) North Holland Publ. Co.