Journal of Crystal Growth **5** (1969) 207–209 © *North-Holland Publishing Co., Amsterdam*

ON THE GROWTH OF LARGE PERFECT CRYSTALS OF SODIUM NITRATE

S. N. KOMNIK and V. I. STARTSEV

Physico-Technical Institute of Low Temperatures, The Ukrainian Academy of Sciences, Kharkov 86, Ukr.S.S.R.

Received 8 August 1968

The production of sodium nitrate single crystals (with dislocation density of about 10^5 cm^{-2}) of 70 mm in diameter and 40 mm in length is described. The crystals were grown by the modified technique of Kyropulos, small plates of single crystal mica (of 20 mm in diameter) being used as a seed. The latter were glued to the cooler – a copper rod (water cooling was not needed). The growing of a crystal was accomplished in an aluminium crucible. The crystals obtained were completely transparent, without cracks, giving good cleavage planes. An etchant – zinc saturated ice acetic acid revealing both the grown-in dislocations and fresh ones – is proposed.

1. Introduction

The paper deals with the production of perfect single crystals of sodium nitrate (dislocation density about 10^5 cm^{-2}) by the modified method of Kyropulos using small plates of single crystal mica as seeds.

In manufacturing optical devices an essential role is now played by polarizing prisms. Up to now prisms of calcite were used for this purpose. Natural reserves of calcite are not large and the problem of growing calcite single crystals has not yet been solved. Sodium nitrate single crystals can be a good substitute for calcite in manufacturing polarising prisms; therefore, it is interesting to investigate the possibility of growing large perfect crystals of this material.

Crystals of sodium nitrate are also interesting for the study of plastic properties because two types of plastic deformation, glide and twinning, take place in these crystals at room temperature and it is possible to investigate their interaction. This requires perfect crystals.

To grow good $NaNO_3$ single crystals is extremely difficult. Firstly, crystals of sodium nitrate have pronounced thermal conductivity anisotropy, the thermal conductivity being a maximum in the direction of the [111] optic axis. The maximum rate of growth proceeds in the same direction when crystals are grown from the melt. As a result, if the direction of the growth does not coincide with the [111] direction, the crystals grow in blocks. Secondly, the anisotropy of the heat expansion coefficient leads to thermal stresses in the blocked single crystals on cooling. This condition is enhanced by the anomalous change of thermal expansion near 275 °C, where the phase transition of the second type takes place[1]). To obtain a perfect unstressed crystal it is apparently necessary to provide the most homogenous conditions for growth. For this the following requirements should be met:

1) the growth axis must coincide with the [111] direction,
2) the crystal must grow without any container,
3) the cooling after annealing must be slow.

The methods of $NaNO_3$ single crystal growth[2–6]), described in the literature, do not allow perfect crystals of large dimensions to be obtained. The reason for this is that in the methods described the above conditions are not all satisfied at the same time. The most acceptable method of growth seemed to be on to floating mica, which serves as an insoluable seed, the axis of growth coinciding with [111] direction. However, the strict requirements for the growth conditions (i.e. the growth is to begin at one point on the mica) and the quality of the seed (the mica plate is to be perfect and of large dimensions), make the method unacceptable.

We used the method of drawing the crystals from the melt (Kyropulos method) using small discs of mica as a seed.

2. Crystal growth

To grow the crystals the crucible furnace of 120 mm in diameter and 200 mm in depth (fig. 1) with the side (1) and bottom (2) heaters was used. The bottom heater has a stabilized voltage supply. The power of the side heater is adjusted by the potentiometer EPD-12. The thermocouple (3), placed near the coil of the side heater, serves as a pickup. The furnace has a cover (4) with two mica windows provided for visibility during growth. In the centre of the cover there is an opening for the cooler (5). A rotating copper rod of 20 mm in diameter acted as the cooler (the water cooling was not required). The crystals were grown in an aluminium crucible (6) of 100 mm in diameter, 150 mm by height and 0.8 mm of wall thickness. As a seed a mica–muscovite plate (7) of 22 mm in diameter and 0.5 mm of thickness was used, it was glued to the edge of the cooler by BF-2. The crystals were grown from the raw material of the grade "chemically pure", which had been preliminarily purified by recrystallization.

The raw material was melted when both heaters were turned on, then more raw material was added into the crucible until the level of the melt reached 1.5 cm from the upper edge of the crucible. The temperature of the melt did not exceed 340 °C as at a higher temperature $NaNO_3$ decomposes. The cooler, with the seed glued on to it, was immersed in the heated melt so that the mica came into contact with the melt. The seed was kept in this position for 30 min. Then the cooler was lifted by 3 mm so as to maintain contact between the mica and the melt, after which the cooler was rotated (rate of rotation 2 rpm) and the temperature was slowly lowered (2 deg/hr) by means of EPD-12, i.e., with the aid of the only side heater, the power of the bottom heater being stable up to the end of the run. In ten hours the crystal grew in diameter to 70 mm, the cooler being raised after this at a rate of 2 mm/hr. Thus the $NaNO_3$ single crystal of 70 mm in diameter and 40 mm in length was grown in about 30 hr. The grown crystal was transported with heated pincers into the furnace for annealing, where it was kept for 4 hr at 270 °C and then the temperature in the furnace was lowered at a rate of 3 deg/hr. The crystals obtained were transparent, uncracked and exhibited good cleavage (fig. 2).

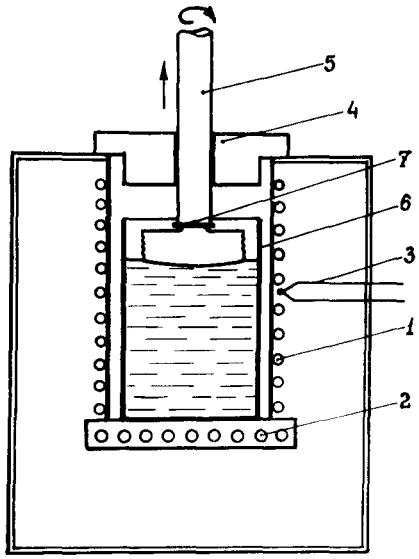

Fig. 1. Diagram of the furnace. (1) side heater; (2) bottom heater; (3) adjusting thermocouple; (4) furnace cover; (5) cooler; (6) crucible; (7) mica seed.

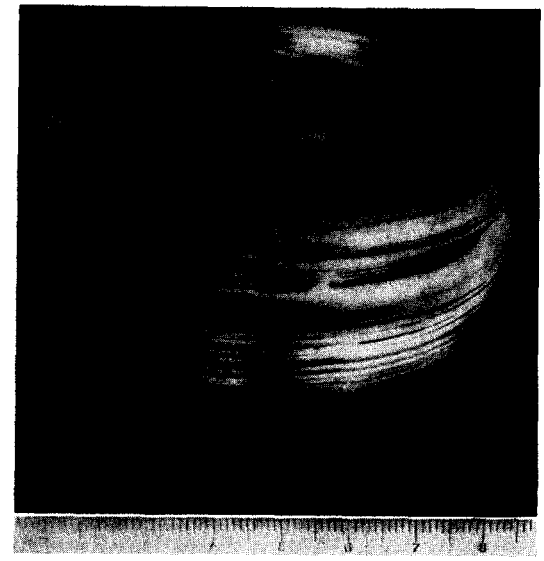

Fig. 2. Grown crystal of sodium nitrate.

To control the perfection of crystals obtained the method of selective chemical etching for dislocations was used. For this purpose an etchant of a zinc saturated ice–acetic acid mixture was chosen. This reveals dislocations on the cleavage plane. The etchant made it possible to observe not only the grown-in dislocations, but the freshly produced ones also. The density of dislocations in crystals grown by the above method was about 10^5 cm^{-2}. The crystals contained a small

number of blocks, giving vicinals on the cleavage plane. The angular misdesorientation of the blocks, typical for such samples, was 40 inch. The etched micrographs of sodium nitrate crystals are shown in fig. 3.

Fig. 3. Dislocations in sodium nitrate. ×200.

References

1) F. C. Kracek, J. Am. Chem. Soc. **53** (1931) 2609.
2) E. Stober, Z. Krist. **61** (1925) 299.
3) H. C. Ramsperger and E. H. Melvin, J. Opt. Soc. Am. **15** (1927) 359.
4) E. V. Tsekhnovitser, Zh. Fiz. Khim. **5** (1934) 1452.
5) C. D. West, J. Opt. Soc. Am. **35** (1945) 26.
6) F. Yamaguti, J. Phys. Soc. Japan **7** (1952) 113.