CRYSTAL GROWTH OF CaF_2

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The method of the processing and the production of CaF_2 singlecrystals doped with rare-earth ions has an essential influence on the spectral characteristic of the material. The contamination by oxygen and by moisture during the growth of the crystal causes a formation of scattering centres undesirable for optical application [1, 2]. There is evidence that the scattering centres are formed of small particles of CaO with a size of about 1 μm. The building-in of sulphur and chlorine into CaF_2 has a similar effect [3]. The decrease of the above mentioned impurities is therefore one of the main pre-requisites in the production of CaF_2 singlecrystals.

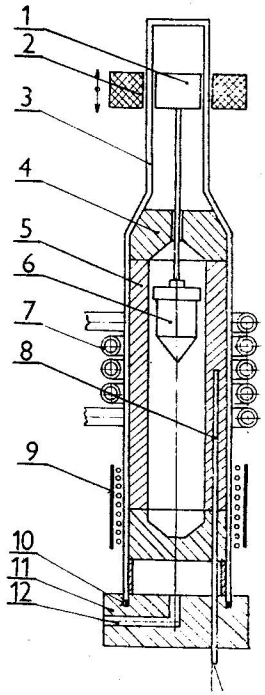

Fig. 1. Device for growing CaF_2 siglecrystals. 1 — ferromagnetic core, 2 — water cooled permanent magnet, 3 — quartz tube, 4 — graphite cover, 5 — graphite tube, 6 – graphite crucible, 7 – R. F. coil, 8 – thermocouple, tube, 9 – additional heating, 10 – rubber gasket, 11 – – water cooled copper stand, 12 – to vacuum.

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It was found that a suitable way for the removal of CaO is to grow the crystal in gaseous HF. One of the disadvantages of this method is the occurrence of bubbles. Their number depends on the HF solubility, the purity of the material, the viscosity of the melt and the growing rate. An improvement can be achieved by a slow growing rate and a high temperature gradient [4]. A simpler way of the removal of CaO is the addition of about 1 % PbF_2 into the raw material. PbO and the remaining PbF_2 still present in the melt after the reaction $PbF_2 + CaO \rightarrow PbO + CaF_2$ are evaporated during the crystal growth [5].

The Stockbarger method of growth which we have used has the following disadvantages: a. only small growing rates are possible; b. graphite, from which the crucibles are made, reacts with some of the doped elements. The growing furnace has been constructed with respect to the agressivity of fluorine and the relatively high temperature. The main parts of the apparatus are shown in Fig. 1. The crucible and all the graphite parts have been made of a spectral grade purity graphite in order to eliminate the contamination by sulphur. The temperature stabilizer guaranteed a temperature stabilization of ± 4 °C at 1450 °C. The additional resistance heating served to set an optimum temperature axial gradient.

The vacuum of 4×10^{-5} torr is a suitable environment for the crystal growth. It is important that the temperature during the long drying of the raw material should not exceed 100 °C. In the reverse case the process of the hydrolysis and of the building-in of OH- into the lattice takes place. The optimum conditions for the crystal growth were as follows: a temperature of 1450 °C for one hour, a shift of 9.4 mm per hour, an axial temperature gradient of 30 °C per cm. The annealing was done by a slow temperature decrease from 1200 °C to room teperature in the vacuum. The final product with a 15 mm diameter and a 35 mm length has not shown a visible ligtht scattering.

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