A STUDY OF THE CRYSTALLIZATION CONDITION FOR MONOCRYSTALS OF ALKALI EARTH ORTHOPHOSPHATES AND TRANSITION METALS FROM MELTS

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INTRODUCTION. Crystallization of the compound $BaM^{II}_2(PO_4)_2$, where $M^{II}=Ni^{2+}, Co^{2+}$ or Mg^{2+}, is not studied in recent literature. In order to obtain monocrystals of these compounds, for which we expect, on the structure basis[1], to possess ferroelecric properties, it is necessary first of all to determine the method and optimal conditions of the crystal growth.

EXPERIMENTAL METHOD. We have used the method of forming the crystal layer on the supercooled crucible wall in order to determine optimal crystal growth rate. The aparatus is shown in Fig.1. Basic parts of the aparatus are: silicon crucible for crystallization (1), electroresistant shamber furnace (2), cooler (3), transformer for continual variation of voltage (4), and thermocoupling (5).

A crucible chemically pure, Fig.1.(1), iz filled with the earlier prepared powder of $BaM^{II}_2(PO_4)_2$ and put in the aparatus as shown in Fig.1. The temperature 1350°C is achieved by a gradual voltage regulation on the ends of the furnace heaters. The sample melts at approximately 1300°C, but in order to get a better homogenization and extraction of possibly remaning gas bubles, the sample is kept for 12 hours at the temperature 1350°C.

Crystallization begins when the cooler on Fig.1.(3) is set into contact with the crucible top and when the air stream is switched on, so that the temperature of the crucible front wall is decreased for 100°C. Therefore the melt begins to solidify from the crucible top down to the other end.

RESULT AND DISCUSSION. Under the crystallization conditions described in the previous section the substances crystallized in the form of a policrystal which consists of monocrystalline grains of different sizes. According to the size of monocrystal grains we distinguish quite clear two different regions. The first is next to the cooler, the

length of which is 6-8 cm (depending on the substances) which have quite small crystal grains, and the second one has considerably larger monocrystal grains, see Fig.2. The position of the border between these two regions is at $BaMg_2(PO_4)_2$ on the 6-th cm from the cooler, at $BaCo_2(PO_4)_2$ on about the 7-th cm, while at $BaNi_2(PO_4)_2$ it stretches on about 8-th cm.

According to B.N.Volfson[2] the rate of solidification of the melt with the above mentioned conditions is given by the following relation.

$$\frac{d\delta}{dt} = \frac{\Delta T}{\alpha \lambda \gamma (\frac{\delta}{2K} + 1)}$$

where δ is the thickness of the solidified layer; t is the time; ΔT is the difference of the melt temperature and the air temperature in the cooler; α is the thermal resistance of the crucible wall next to the cooler; λ is the latent heat of the melting of the substance; γ is the specific weight of the substance; K is the thermal coductivity of the crystal.

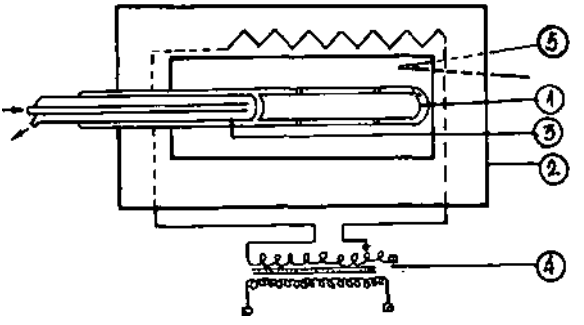

Fig.1. Apparatus scheme used for the crystalization of the described substances

Fig.2.Monocrystal grains from the second region

From this relation we see that the rate of solidification is greatest at the beginning of the crucible (δ=0) and gradually decreases towards the other end of the crucible.However, for the crystal growth it is necessary that the rate of solidification should not be larger than the maximum linear rate (R_g) which is characteristic for

each substance.

Based on this observation it is possible to explain the origin of two regions in the crucible. In the first region of the crusible $\frac{d\delta}{dt} > R_g$, in the second region $\frac{d\delta}{dt} < R_g$, on the border between these two regions $\frac{d\delta}{dt} = R_g$. In the second region of the crucible $\frac{d\delta}{dt} < R_g$ not one monoc - rystal, but more, are obtained because the temperature gradient is small. Therefore the nucleation of parasite crystals appears in front of the crystallization line.

According to A.B.Bekturov et al. [3] the large rate of crystallization (large R_g) is characteristic for those phosphates where the binding between cations and anions has a high degree of ionicity. Our results are in qualitative agreement with the fact that the binding Mg-O 29%, Co-O 35% and Ni-O is 41% covalent.[3] The binding Ba-O is only 14% covalent and this makes the crystallization of these compounds easier.

References

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