YU ISSN 0015—3206
FZKAAA 22 (3) 497 (1990)

LETTER TO THE EDITOR

CRYSTALLIZATION OF $BaNi_2(PO_4)_2$

BRANISLAV ČABRIĆ[+], BOŽIDAR ŽIŽIĆ[++], MILAN LJ. NAPIJALO[++] and TOMISLAV PAVLOVIĆ[+++]

[+]*Institute of Physics Faculty of Natural Sciences and Mathematics, P. O. Box 60, 34001 Kragujevac, Yugoslavia*

[++]*Faculty of Physics, Faculties of Natural Sciences and Mathematics, Beograd, Yugoslavia*

[+++]*Faculty of Philosophy, Department of Physics, Niš, Yugoslavia*

Received 12 August 1989

Revised manuscript received 12 February 1990

UDC 539.91

Original scientific paper

Crystallization was performed by simplified Stober method. Monocrystal plates, whose size was $50 \times 50 \times 0.5\,mm^3$ were obtained. The shape and size of monocrystal grains were explained on the basis of the crystal structure $BaNi_2(PO_4)_2$ and physical conditions during the process of crystallization.

The compound $BaNi_2(PO_4)_2$ was first sythesized in 1968[1], and also determined the crystal structure by the X-ray powder diffraction method. The layered arrangement of various ions in the structure should be the cause of pronounced anisotropy of physical properties. These expectations were partially confirmed by studying magnetic properties[2,3]. B. Čabrić et al.[4] have studied crystallization of these compound. During this investigation, was found that $BaNi_2(PO_4)_2$ crystallizes from the melt in the form of small plates.

The purpose of the work reported herein was to produce larger and better quality crystals for testing their physical properties. Since $BaNi_2(PO_4)_2$ crystallizes from the melt in the form of plates[4], the crystallization was performed by Stober method[5].

The apparatus, of simplified modification of the Stober method, is schematically represented in Fig. 1. Main parts of apparatus are crystallization crucible (1), electrical resistance chamber furnace (2), air cooler (3), continuously variable voltage transformer (4) and thermocouple (5). The crucible was made of quartz glass. Vertical temperature gradient is set up in the crucible by means of the air

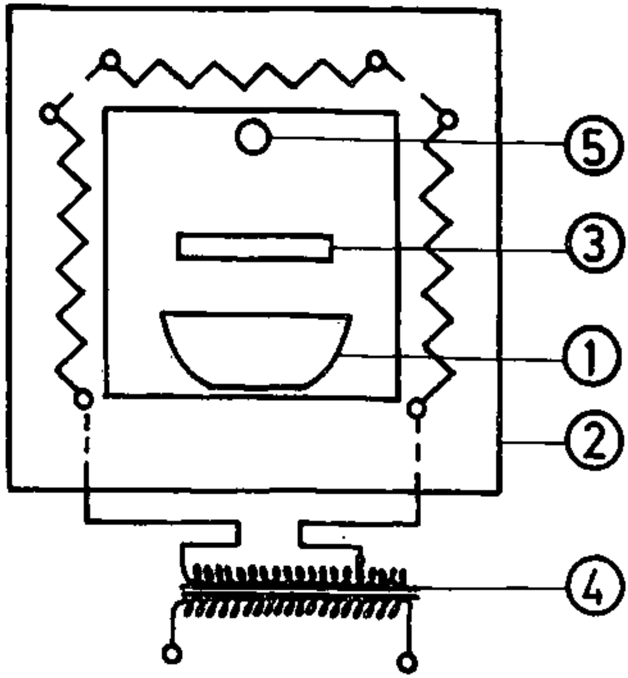

Fig. 1. The crystallization apparatus.

cooler (Fig. 2). The crystallization is performed by shifting the crystallization isotherm temperature vertically downwards, which in turn is accomplished by reducing temperature in the furnace.

The crystallization rate $R\left(=\frac{dl}{dt}\right)$ depends upon temperature gradient $G\left(=\frac{dT}{dl}\right)$ and upon temperature decrease rate $\left(\frac{dT}{dt}\right)$ in the furnace, in the following way:

$$R = \frac{\frac{dT}{dt}}{G}. \qquad (1)$$

It is seen from the above relation that for small crystallization rates one needs high temperature gradient and low temperature decrease rate in the furnace. This relation makes it possible to calculate crystallization rate, given temperature gradient and furnace temperature decrease rate.

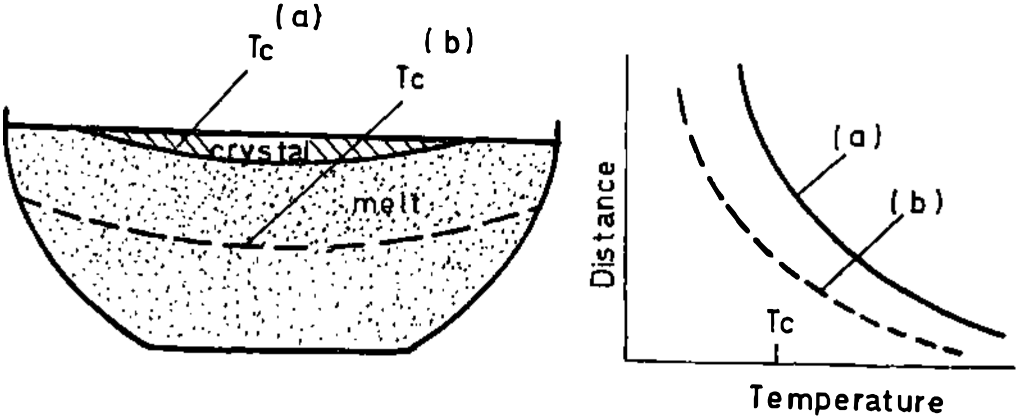

Fig. 2. Shifting of the crystallization temperature isotherm by furnace temperature reduction. (a) and (b) — temperature distribution in the crucible along the vertical in the moments t_a and t_b ($t_a < t_b$), T_c — crystallization temperature, $T_c^{(a)}$ and $T_c^{(b)}$ — crystallization temperature isotherms in the crucible in the moments t_a and t_b.

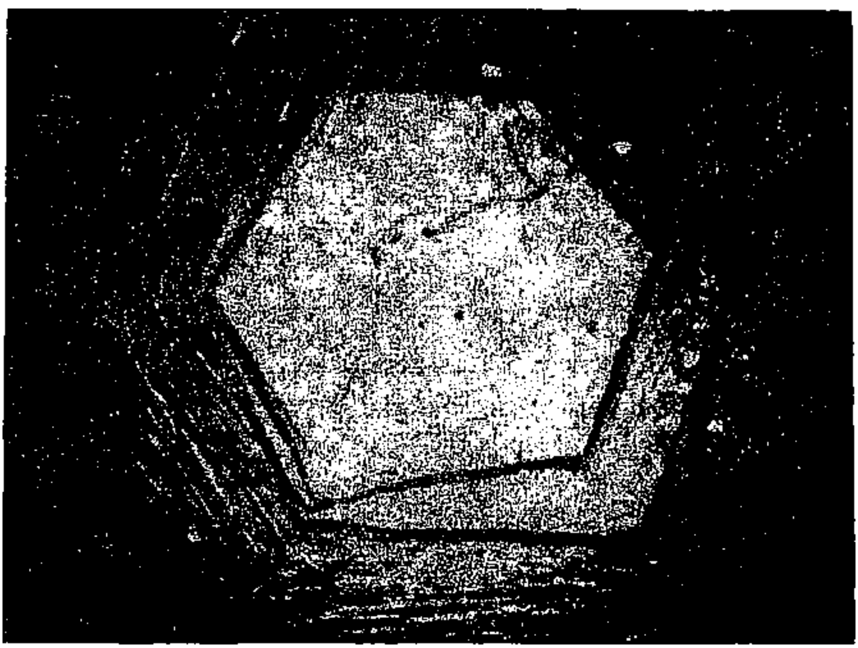

Fig. 3. Monocrystal plates of $BaNi_2(PO_4)_2$ produced on the surface melt at furnace cooling rate of 6 °C/h (magnification 7 ×).

Chemically cleaned crucible is filled with 100 g of $BaNi_2(PO_4)_2$ polycrystal powder synthesized in accordance with Eymond-Laritaz[1]. After 12 hours, temperature of 1350 $\pm$ 10 °C is reached, at which the sample is fully melted. For better homogenization and separation of possibly remained gases, the melt was held 12 to 20 hours at the above temperature. After steady-state was attained in the furnace, and the melt homogenized, crystallization was performed by reducing furnace temperature at a rate of 6 °C/h within the range from 1350 to 1100 °C. Further cooling of the sample proceeded at a rate of 30 °C/h down to room temperature.

At the above conditions $BaNi_2(PO_4)_2$ crystallized in the form, of polycrystals, composed of monocrystal »grains« in the form of plates. The largest and most perfect monocrystal plates formed at the surface melt (Fig. 3), probably because of the highest temperature gradient, from which also follows the lowest crystallization rate (relation (1)).

Exceptionally developed monocrystal plates are parallel to the crystallographic planes (001), which is probably the consequence of the layered crystal structure (Fig. 4). Characteristic hexagonal islands on these surface (Fig. 3) originate from the hexagonal network formed by the nickel ions in the planes (001). Plate-like

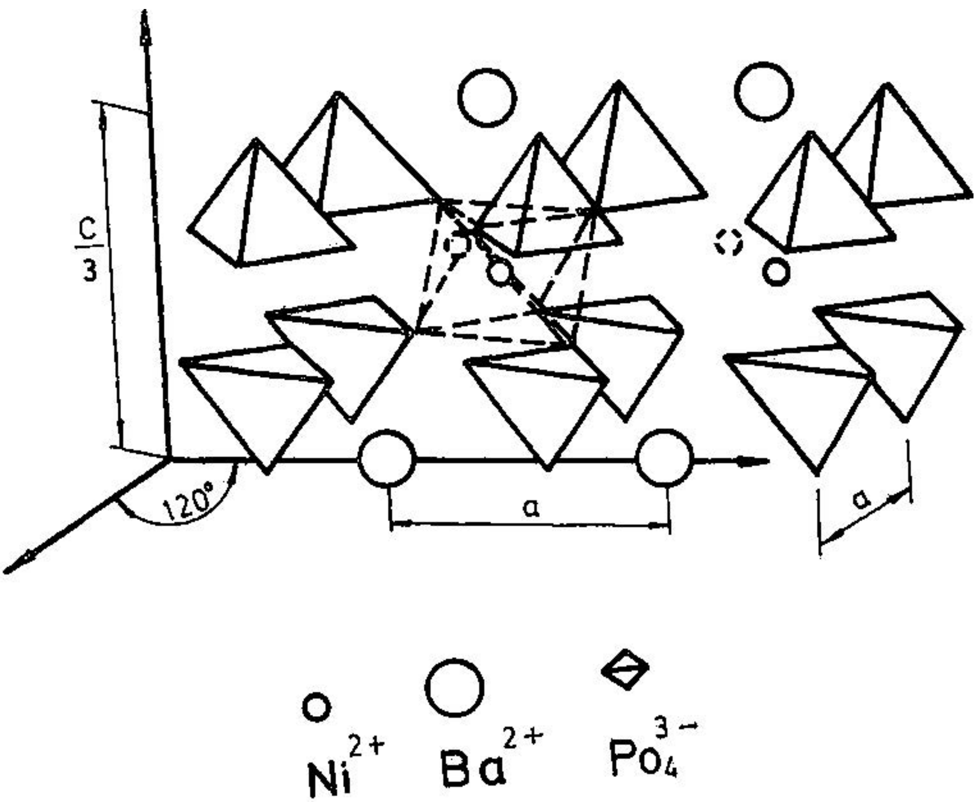

Fig. 4. Crystal structure of $BaNi_2(PO_4)_2$.

form of the monocrystal grains may be explained by the crystal structure in the following way: In order for the seed of crystal to grow in the crystallographic direction [001], it is necessary to periodically insert in single-ion layers Ni^{2+}, PO_4^{3-} and Ba^{2+}. The PO_4^{3-} ion should assume certain orientation that should also periodically change in the direction [001]. Due to this, the seed growth rate, i. e. the monocrystal dimensions, in the direction [001] is very small[6].

In order to obtain monocrystals (plates) of higher thickness it is necessary to commence crystallization on a ready seed, positioned such that the crystallization direction [001] is perpendicular to the isothermal surface of crystallization temperature. Due to low rate of crystal growth in the direction [001], one needs low velocity of crystallization isotherm displacement, i. e. low furnace temperature decrease rate and large temperature gradient (relation (1)). Because of high crystallization temperature of $BaNi_2(PO_4)_2$, this is very hard to achieve.

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KRISTALIZACIJA $BaNi_2(PO_4)_2$

BRANISLAV ČABRIĆ+, BOŽIDAR ŽIŽIĆ++, MILAN LJ. NAPIJALO++ i TOMISLAV PAVLOVIĆ+++

+*Institut za fiziku, Prirodno-matematički fakultet, p. p. 60, 34001 Kragujevac*

++*Fizički fakultet, Prirodno-matematičkih fakulteta, Beograd*

+++*Filozofski fakultet, Odeljenje za fiziku, Niš*

UDK 539.91

Originalni naučni rad

Kristalizacija je vršena pomoću uprošćene Stober-ove metode. Dobijene su monokristalne pločice dimenzija $50 \times 50 \times 0{,}5\,mm^3$. Oblik i veličina monokristalnih zrna objašnjen je na osnovu kristalne strukture $BaNi_2(PO_4)_2$ i fizičkih uslova pri kristalizaciji.