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Phase equilibria and β -BaB₂O₄ crystal growth in the Ba, Na, B // O, F system

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Due to the phase transition at 925°C, nonlinear optical crystals of low temperature modification of β -BaB₂O₄ (BBO) are commonly grown from high-temperature solution by top-seeded solution growth technique. Main solvents are some compositions in the BaO-B₂O₃-Na₂O ternary system, the BaB₂O₄ – NaF system, the BaB₂O₄ – BaF₂ system and also some mixed sodium oxide-fluoride compositions. The information in the available literature has been often contradictory and segmental. We believe that it's more appropriate to consider mentioned solvents as one four-component mutual system Ba, Na, B // O, F. It represents a trigonal prism with the corresponding oxide (BaO-B₂O₃-Na₂O) and fluoride (BaF₂-BF₃-NaF) concentration triangles at the bases.

Our investigation of the BaB₂O₄ – NaF system has shown that it includes a primary crystallization area of the new compound Ba₂Na₃[B₃O₆]₂F (hexagonal system, *P*6₃/*m*, *a*=7,346(1) Å, *c*=12,637(2) Å) [1,2]. Faceted bulk crystals of the new compound have been grown. Thus, BaB₂O₄ – NaF section belongs to the Ba, Na // BO₂, F (BaB₂O₄–(NaBO₂)₂–(NaF)₂–BaF₂) ternary mutual system, which is the prism section. Comprehensive investigation of the phase equilibria and crystal growth has been carried out. It has been shown that the BaB₂O₄–Ba₂Na₃[B₃O₆]₂F system is suitable for BBO crystal growth. The fast pyrohydrolysis of BaF₂ in air causes gradual transformation of the BaB₂O₄–BaF₂ system into the BaB₂O₄–BaO system and results in the co-crystallization of BaB₂O₄ and Ba₂B₄O₁₁ phases, making the growth of large high-quality β -BaB₂O₄ crystals in air impossible [3]. The Ba₃B₄O₁₁ phase (PDF 00-058-0115) was earlier found in the BaO-B₂O₃-Na₂O system [4].

High-quality crystals of about 400 g in weight with the convex form of the crystallization front, which is an evidence of the stability of the crystallization process, are reproducibly obtained. Currently the maximum aperture of NLO element cut from the crystals is 30 x 30 x 6 mm³ [5].

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Transition metal sheet-like systems based on diacetic ligands

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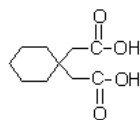
The preparation, the structure determination by means of X-ray

diffraction and the study of magnetic properties of different transition metals sheet-like systems based on diacetic ligands have been done.

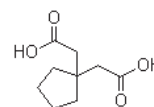
1,1-Cyclohexanediactic and 1,1-cyclopentanediacetic acids, dicarboxylic acid-substituted C-6 and C-5 alicyclic hydrocarbons, can exhibit typical carboxyl group chemistry in variety of industrial applications. There are almost infinite esters obtained from thousands of potential starting materials. Esters are formed by removal of water from an acid and an alcohol, e.g., carboxylic acid esters, phosphoric acid esters, and sulfonic acid esters. Carboxylic acid esters are used as in a variety of direct and indirect applications. Lower chain esters are used as flavouring base materials, plasticizers, solvent carriers and coupling agents. Higher chain compounds are used as components in metalworking fluids, surfactants, lubricants, detergents, oiling agents, emulsifiers, wetting agents textile treatments and emollients.

Both acids are metal chelators. Chelation is applied in metal complex chemistry, organic and inorganic chemistry, biochemistry, and environment protection. It is used in chemotherapeutic treatments for metal poisoning. An example of end product derived from 1,1-cyclohexanediactic acid is gabapentin, an anti-epileptic agent, chemically described as 1-(aminomethyl)cyclohexane acetic acid.

Polynuclear compounds of high-spin cobalt(II) ions bridged by carboxylate groups exhibit different magnetic behaviors depending on the bridging mode of the carboxylate and on its coordination number [1-3]. Concerning the magnetic properties, a relationship between the nature of the magnetic coupling and the type of bridge that links the metal center has been proposed.



1,1-Cyclohexanediactic acid



1,1-Cyclopentanediacetic acid

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Keywords: crystal engineering, X-ray diffraction, magnetic properties

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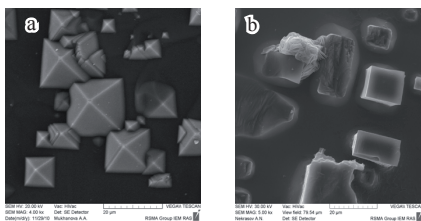
Peculiarities of crystal growth and morphology of carbonate-synthetic diamonds

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Diamond formation in multicomponent K-Na-Ca-Mg-melts oversaturated with dissolved carbon in respect to diamond is studied at 7.0 – 8.5 GPa. Experiments on diamond spontaneous crystallization and seeded growth were carried out in the “anvil-with-hole” high-pressure apparatus. Diamond-forming processes are high-effective [1] and characterized by estimated density of nucleation of no less than 3 – 5•10³nuclea in cm³ for individual crystal of up to 200 μm size, spinel-law and polysynthetic twins, polycrystalline aggregates of

Poster Sessions

up to $1 \cdot 10^3$ nuclei in cm^3 . The aggregates are similar to the natural “diamondite” type and consist of microcrystals sized from 10-20 nm to 50-100 μm . Composition of the experimental growth carbonate melt-carbon solutions is chemically similar to the natural parent medium [2] that determines the physicochemical mechanism of the “carbonate-synthetic” diamond formation and, respectively, peculiarities of the face growth and morphology. By kinetic indication, it is possible to determine regions (1) of spontaneous nucleation and crystallization of diamond (“region of labile carbon oversaturation”) and (2) of diamond seeded growth (“region of metastable carbon oversaturation”) within the PT region of diamond thermodynamic stability. A boundary between the two regions is positioned of less than 0.5 GPa to the diamond-graphite equilibrium lines creating a narrow region of diamond seeded growth between the boundaries. Within the diamond-seeded growth region, morphological peculiarities of growing faces and crystallization steps and fronts are kinetically-dependent. The crystallization fronts are variable from polycentric and roughly blocked to smooth with nano-dimensional growth steps. The interaction of crystallization fronts can impose the effects of the layers overgrowth. All the new growing layers, independently of the seed face (111) with smooth layers or (100) with semi-octahedral hills, have the “octahedral” orientation for growth layers (fig. a). The “cubic” morphology demonstrated in the fig. b is firstly obtained; it is important that the orientation of the growing layers in the case is “cubic”. This uncommon result is obtained at highest temperature of 2400°C.



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Keywords: carbonate-synthetic diamond, morphology, seeded growth

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Synchrotron topography of (Nb,Yb):RbTiOPO₄ single crystals and related materials

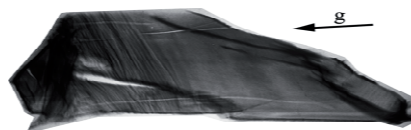
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Rubidium titanyl phosphate, RbTiOPO₄ (RTP) is isostructural with the well-known potassium titanyl phosphate, KTiOPO₄ (orthorhombic, Pna2₁). Its non-linear optical properties make it suitable as a frequency doubling material when doped with active lanthanide ions such as Yb³⁺ [1]. However, the distribution coefficient of Yb³⁺ in RTP crystals is very low and the codoping with Nb⁵⁺ is required to increase the concentration of Yb³⁺ in the crystals through a mechanism of electrical

compensation of the matrix [2]. Laser action has been demonstrated at $\sim 1 \mu\text{m}$ for these crystals [3]. The (Nb,Yb):RTP crystals are grown by the top-seeded solution growth (TSSG) technique using self-fluxes to avoid the presence of undesired ions in the solution that can affect the physical properties of the crystals. However, the crystals exhibit a tendency to crack during removal from the furnace after growth. Such cracked crystals are obviously not suitable for optical and spectroscopic applications.

Synchrotron white beam X-ray topography (SWBXT) has been employed to characterize the structural defects in these crystals to investigate the cause of cracks. X-ray topographs recorded from both doped and undoped crystals reveal defect features such as growth striations, growth sector boundaries, dislocations, grain boundaries, and especially, inhomogeneous strain that might be responsible of cracking. The distribution of these defects have been mapped in each type of crystal along the three main crystallographic directions and compared. Defect distribution was also analyzed with respect to the growth conditions in order to gain insights into the growth mechanism and the origin of cracks. Results from these studies will be presented.

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Keywords: synchrotron white beam X-ray topography, top-seeded solution growth, RbTiOPO₄

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The CrystalHarp™ - an advanced high throughput capillary plate for protein crystallization

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Counter diffusion crystallization in capillary is an easy, cost-effective and practical procedure for obtaining protein crystals for *in situ* X-ray data analysis. This method is used simultaneously for screening, incorporation of heavy atoms and cryo protection in a single capillary [1], [2].

We present a novel capillary crystallization plate, based on the counter-diffusion method and designed for 48 high throughput-screening experiments. Due to the plate's design only 20 μl of protein is needed to load the plate very quickly. A liquid handling robot can facilitate the pipetting of the individual well conditions. The crystallization plate is compatible with any incubation and imaging systems and allows *in situ* X-ray diffraction measurements. Alternatively, an individual capillary can be removed from the CrystalHarp™ and the crystal can be analysed 360° *in situ* by X-ray diffraction.

For initial plate validation, crystallization experiments with six commercially available soluble proteins, two soluble in-house proteins