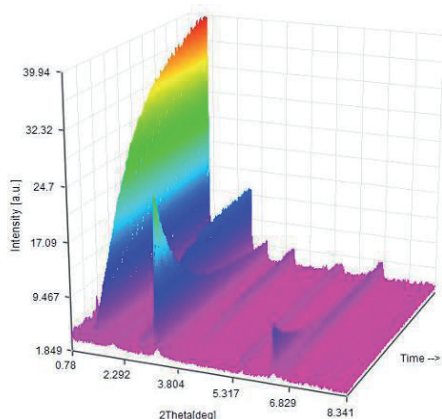


nanocomposites, carried out by crystallographic and thermogravimetric techniques, revealed that this synthesis yield is comparable to that of standard methods but with time, solvent, and energy saving advantages. Moreover, the in situ diffraction experiments allowed us to shed some light on the kinetics of the intercalation process with sub-second resolution and the parameters affecting the reaction.



[1] M. Milanesio, E. Conteroso, D. Viterbo, L. Perioli, G. Croce, *Cryst. Growth Des.*, **2010**, *10* (11), 4710-4712.

**Keywords:** intercalation, in-situ, XRPD

## MS49.P04

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### Crystallogenic Grounds of Isomorphism

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Crystallogeny of solid solutions (mixed crystals) should be singled out as a special field due to a complex of phenomena beyond the scope of an ordinary growth process and due to some problematic aspects like controlling isomorphous composition [1]. The principal specificity of mixed crystal formation (in contrast to that for crystals of a fixed composition) is a permanent exchange of isomorphous components between a crystal and solution, which accompanies any process. The mechanism is a combination of dissolution of unstable surface configurations with autoepitaxial overgrowth of stable ones; the appropriate surface spots spread on the surface in a manner of chaotic micro-mosaic. The monocrystallinity is kept due to the autoepitaxial overgrowth. Survival of stable surface configurations is the main factor of controlling crystal composition ("ensemble mechanism").

Such a process runs in two the ways dependently on the substance solubilities. A volume-deficit exchange runs when the crystal substance solubility is higher than the dissolved substance solubility. It is fast and causes implanting inclusions into a continuous crystal matrix (these are either inclusions of the medium solution in ternary systems or of solid phases in quaternary and more complex systems). A volume-excess exchange runs when the crystal substance solubility is lower than the dissolved substance solubility. It is slow and causes excrescences onto the crystal surface. The reaction runs by itself at isothermal conditions as well as in a combination with direct crystal growth at supercooling and with dissolution at overheating.

A metastable heterogeneous equilibrium between a crystal and compositionally foreign solution becomes settled at a supercooling of the value determined by the phase compositions (it should be noted that the quantitative indication of supersaturation is not available for such systems and using supercooling is needed). This is important factor for the component selection causing a tendency of a bimodal distribution

of precipitated units of nano- and micro-scales in composition, but the distributions are blurred due to a dispersion of local conditions. Different habits of overgrowing spots indicate a variation of their composition. Such spots are buried under new layers causing a chaotic isomorphous inhomogeneity of the bulk that is typical for such crystals.

Compositions of spontaneously precipitated crystals are also of a bimodal distribution, which character depends on supercooling in spite of supercooling does not effect on the total composition. Substantially, the bimodality is related to that of the precipitate distribution in grain sizes. This shows a complicated connection between crystal composition, supercooling and growth kinetics caused probably by an interaction of growth and isomorphous exchange as well as a solution inhomogeneity.

The described behavior of crystals was observed in situ and ex situ in numerous soluble ternary systems like  $(\text{Pb},\text{Ba})(\text{NO}_3)_2\text{-H}_2\text{O}$ ,  $(\text{Co},\text{Ni})(\text{NH}_4)_2(\text{SO}_4)_2\cdot 6\text{H}_2\text{O-H}_2\text{O}$ ,  $(\text{K},\text{Rb})\text{HC}_8\text{H}_4\text{O}_4\text{-H}_2\text{O}$ ,  $(\text{Mg},\text{Ni})\text{SO}_4\cdot 7\text{H}_2\text{O-H}_2\text{O}$ ,  $\text{K}_2(\text{Cr},\text{S})\text{O}_4\text{-H}_2\text{O}$ , and  $\text{K}(\text{Cl},\text{Br})\text{-H}_2\text{O}$ , as well as in quaternary ones  $(\text{Co},\text{Fe})\text{SO}_4\cdot 7\text{H}_2\text{O-NH}_4\text{SO}_4\text{-H}_2\text{O}$  and  $\text{K}_2(\text{Cr},\text{S})\text{O}_4\text{-KCl-H}_2\text{O}$ . Methods of optical microscopy, atomic force microscopy, X-ray microtomography, X-ray diffractometry, microprobe analysis were used. Concentration phase diagrams were modified into nomograms for the interpreting basis.

To a conclusion, the presented concept is a substantial part of the crystal growth generalization for polyphase systems [1].

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**Keywords:** crystallogeny, isomorphism, exchange

## MS49.P05

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### Anomalous structure and structure reconstructions of nano-dispersed powders of rare-earth oxides and fluorides produced from amorphous precursors

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The nano-dispersed rare earth simple oxides  $\text{Lu}_2\text{O}_3$ ,  $\text{Gd}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$  and  $\text{Eu}_2\text{O}_3$ , garnets  $\text{Y}_3\text{Al}_5\text{O}_{12}$  and  $\text{Y}_3\text{Ga}_5\text{O}_{12}$ , perovskites  $\text{YAlO}_3$  and  $\text{LaAlO}_3$ , borates  $\text{LuBO}_3$ ,  $\text{GdBO}_3$ ,  $\text{LaBO}_3$  and  $\text{YBO}_3$ , molybdates  $\text{Eu}_2(\text{MoO}_4)_3$  and  $\text{Gd}_2(\text{MoO}_4)_3$  and fluorides  $\text{LuF}_3$  and  $\text{Na}_5\text{Lu}_9\text{F}_{32}$  were produced from amorphous precursors. X-ray investigations have shown that independently of precursor method synthesis the first stages of crystallisation of such compounds are characterized by new four phenomena.

First phenomenon consists in formation of very unusual two-phase state in simple rare earth oxides  $\text{R}_2\text{O}_3$ , garnet  $\text{Y}_3\text{Ga}_5\text{O}_{12}$  and  $\text{Na}_5\text{Lu}_9\text{F}_{32}$  at early stages of the nano-crystallites formation. These phases are isomorphous and have different lattice parameters. Detailed x-ray and high resolution electron microscopy investigations have shown that both phases are realized in the same crystallite and correspond to surface and core phases. The surface phase has enlarged lattice parameters with respect to core phase parameters. This two-phase state transforms then into one-phase state in process of crystallites growth. Such two-phase states was also produced in micro-dispersed  $\text{LuBO}_3$  and  $\text{Eu}_2(\text{MoO}_4)_3$  after a long milling of the powders.

The second phenomenon is phase reversibility. It means that the phase sequence known for macro-sized powders at temperature increasing is reversible for nano-sized grains. For example, for macro-sized powders of  $\text{Eu}_2(\text{MoO}_4)_3$  low temperature phase is  $\alpha$ -phase. It undergoes phase transition into  $\beta$ -phase at 800 C. In process of annealing of the precursor of  $\text{Eu}_2(\text{MoO}_4)_3$  the phase sequence is as follows:  $\beta$ -phase  $\rightarrow$   $\alpha$ -phase  $\rightarrow$   $\beta$ -phase again. The same is observed

for  $\text{LuBO}_3$  in process of annealing of the amorphous precursors: high vaterite phase  $\rightarrow$  calcite phase  $\leftrightarrow$  high vaterite phase again instead of the previously known sequence: calcite phase  $\leftrightarrow$  high vaterite phase. For  $\text{LaBO}_3$  instead of sequence: aragonite phase  $\leftrightarrow$  monoclinic phase in micro dispersed powders we have the sequence: monoclinic phase  $\rightarrow$  aragonite phase  $\leftrightarrow$  monoclinic phase if the crystallization is realized from amorphous precursor.

The third phenomenon consists in acceleration of the phase formation at lower temperature and for shorter time if temperature of the sample under synthesis is increased continuously. Such effect was observed in process of borates  $\text{RBO}_3$  and garnets  $\text{R}_3\text{M}_5\text{O}_{12}$  synthesis. It was established that the initiating effect of the continuous heating on synthesis of the garnets, which have cubic structure for all R-atoms only, is realized in more rapid growth of the crystallites from nano- to micro-sizes. For the borates which have a few different phases in dependence of R-atom used the continuous heating brings to formation together with equilibrium phase the new phases known for other rare earth elements.

The fourth phenomenon is the effect of "structure infection". Such effect was observed at first stages of  $\text{YBO}_3$  crystallization after adding a few percents of Sc atoms in amorphous precursor. In this case calcite phase of  $\text{YBO}_3$  is formed. However it is unknown for yttrium borate but is stable phase for  $\text{ScBO}_3$ . Almost the same situation is observed in the process of  $\text{YAIO}_3$  perovskite phase synthesis. The hexagonal phase of  $\text{YAIO}_3$  can to form at first steps of crystallization ( $T \sim 600$  C) after adding a small amount of  $\text{La}_2\text{O}_3$  (hexagonal structure) in amorphous precursor while such phase is known in micro-dispersed state at  $T > 1400$  C only.

**Keywords:** nanocrystal, rare-earth compound, X-ray

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**Improvement of crystal qualities by solution stirring techniques**  
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Solution stirring techniques are effective to make crystals with high quality, and widely introduced in industrial field. We have succeeded in growing high quality  $\text{CsLiB}_6\text{O}_{10}$  and DAST by utilizing solution stirring techniques.<sup>1</sup> These results show that availability of the stirring techniques covers not only inorganic materials but also organic materials. In this presentation, we will introduce effects of solution stirring on GaN crystals and some protein crystals (hen-egg white lysozyme (HEWL) and glucose isomerase (GI)). Comparison of these results will show some mechanisms how the solution stirring techniques improve the crystal qualities.

We introduced sodium flux method to grow GaN single crystals.<sup>2</sup> Using this method, GaN can be grown by the dissolution of pressurized nitrogen gas into Ga-Na melt under conditions of approximately  $\sim 1143$  K and 3.4 MPa. Growth condition easily becomes unhomogeneous in a crucible, then some problems such as unfavorable nucleation, non-uniform crystallization on templates and low yield happen. We must comprehend and control solution conditions to reduce these problems. As a first step we investigated a condition in a crucible. To know the condition distribution in the crucible, we grew some of GaN crystals concentrically in the crucible. A main parameter was solution stirring, that is (1) no stirring, (2) stirring by rotation of a chamber, (3) stirring by fluctuation of a chamber. Sizes, morphologies and surface conditions of these grown crystals reflect a distribution of the supersaturation. As a result, both of the stirring techniques effectively suppress unfavorable

nucleation and achieve faster growth rate than no stirring system. Furthermore solution stirring improved polycrystals and skeletal crystals. These results are obvious evidences for homogenized solution conditions.

In the field of crystallography of protein crystals, crystallographers must consider many conditions and usually use a protein solution of less than  $10 \mu$  in each batch. Thus we applied specially designed rotary shaker to introduce stirring in protein crystal growth. Crystallization plates were set on the rotary shaker, and stable solution flow arose in each batch.<sup>3</sup> In the case of protein crystal growth, surface kinetics can be a late-determining process in many cases, because of the difficulty of accurate molecules rotation and incorporation into crystals. Actually shapes of crystals with or without stirring were almost same in both the case of HEWL and GI. However, densities of defects were strongly affected by solution stirring. The defects densities were estimated by crystal etching. Two kinds of etch pits on HEWL and GI crystals were observed after etching. One is a shallow pit, which indicates the micro defects such as impurities or holes,<sup>4</sup> and the other is deep pit, which indicates the dislocations in crystals. The shallow pits' density tended to decrease with stirring speed. This tendency implies that transportation of impurities, which can be the micro defects, to crystal surface is suppressed by solution stirring. We have succeeded to improve the quality and size of some protein crystals by introducing the stirring method.<sup>5</sup> The decrease of shallow pit density probably is a contribution factor for crystal quality improvement.

As seen above, the way to stir solution and main effects of stirring depend on materials. In the case of GaN crystals, stirring contributed to uniformize solutions in crucible, and in the case of protein crystals, the decrease of micro defects was a main effect of stirring. However, we would like to emphasize that solution-stirring techniques finally improved crystal qualities. Solution stirring is one of a universal principle that is applicable to various materials.

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**Keywords:** solution stirring, GaN, protein crystal

## MS49.P07

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**Mechanical property measurements of growing lysozyme crystal by atomic force microscopy with laser confocal differential interference microscopy**

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We have studied combination of optical microscopy (OM) and atomic force microscopy (AFM). One of the combinations was the seamless observation of OM and AFM [1]. We observed the surface of a potassium dihydrogen phosphate (KDP) crystal by transmission optical microscopy, the laser confocal differential interference microscopy (LCM-DIM, [2]), and AFM. In that study, the LCM-DIM played important role as an intermediary because of its high z-axis resolution. Another study was about the interferometric microscopy using AFM cantilever. We demonstrated the observation of growing steps with measuring the step height [1]. In addition, we also demonstrated measurement of refractive index of pure water by measuring the distance between the interference fringes [3]. The point was its measurement area, which was about 10-micrometer-square region. In this study, we focused on measurements of mechanical