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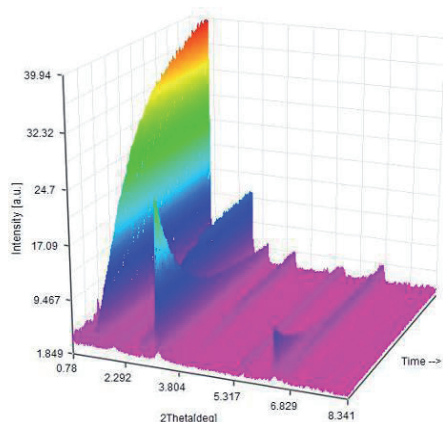
[1] M. Milanesio, E. Conterosito, D. Viterbo, L. Perioli, G. Croce, *Cryst. Growth Des.*, **2010**, *10 (11)*, 4710-4712.

Keywords: intercalation, in-situ, XRPD

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Crystallogenetic 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 isomorphic composition [1]. The principal specificity of mixed crystal formation (in contrast to that for crystals of a fixed composition) is a permanent exchange of isomorphic 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 isomorphic 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 isomorphic 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 $(Pb,Ba)(NO_3)_2$–H_2O, $(Co,Ni)(NH_4)_2(SO_4)_2 \cdot 6H_2O$–$H_2O$, $(K,Rb)HC_8H_4O_4$–H_2O, $(Mg,Ni)SO_4 \cdot 7H_2O$–H_2O, $K_2(Cr,S)O_4$–H_2O, and $K(Cl,Br)$–H_2O, as well as in quaternary ones $(Co,Fe)SO_4 \cdot 7H_2O$–NH_4SO_4–H_2O and $K_2(Cr,S)O_4$–KCl–H_2O. 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 interpretating basis.

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

[1] A. Glikin, *Polymineral-Metasomatic Crystallogenesis, Springer*, **2009**.

Keywords: crystallogeny, isomorphism, exchange

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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 Lu_2O_3, Gd_2O_3, Y_2O_3, La_2O_3 and Eu_2O_3, garnets $Y_3Al_5O_{12}$ and $Y_3Ga_5O_{12}$, perovskites $YAlO_3$ and $LaAlO_3$, borates $LuBO_3$, $GdBO_3$, $LaBO_3$ and YBO_3, molybdates $Eu_2(MoO_4)_3$ and $Gd_2(MoO_4)_3$ and fluorides LuF_3 and $Na_5Lu_9F_{32}$ 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 R_2O_3, garnet $Y_3Ga_5O_{12}$ and $Na_5Lu_9F_{32}$ 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 $LuBO_3$ and $Eu_2(MoO_4)_3$ 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 $Eu_2(MoO_4)_3$ low temperature phase is α-phase. It undergoes phase transition into β-phase at 800 C. In process of annealing of the precursor of $Eu_2(MoO_4)_3$ the phase sequence is as follows: β-phase → α-phase → β-phase again. The same is observed

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