

On the Genetic Nature of Isomorphism: Mechanism of Component Selection during Crystal Growth

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Abstract—The concept of mixed-crystal formation, which has developed since the early 1980s, suggests the leading role of the metasomatic exchange between the crystal and solution. Compositions of solid and liquid phases shift to meet one another up to achieving thermodynamic equilibrium. This mechanism provides the regulation of the crystal composition during the process of isomorphism. The principles of the proposed assembly mechanism of selecting isomorphic components in the proportions dictated by a given combination of conditions (composition of the solution, supercooling or superheating, and temperature) are set forth as follows. The particle assemblages characterize a certain statistical distribution by the composition precipitate on the surface. Only those assemblages, which satisfy the aforementioned conditions, survive, whereas the other assemblages are dissolved, initiating the salting-out of the former assemblages. The validity of the proposed model is corroborated by the development of the assembly structure of autoepitaxial $(K,Rb)HC_8H_4O_4$ nuclei on a $KHC_8H_4O_4$ crystal observed with a Park CP atomic force microscope. The nuclei are widely scattered in composition, degree of faceting, and size, demonstrating their different stability and growth rate. Another example is the distribution of spontaneously precipitated mixed $K(Br,Cl)$ crystals by isomorphic composition and size. The small and large fractions are enriched in KBr in comparison with medium-size fractions, while the volumetric proportions of the fractions reveal a bimodality with the complete absence of fractions 30–50 μm . The traditionally discussed statistical selection of particular ions, which is probably second in importance; however, it may become crucial when the amount of one of the isomorphic components is rather small. While oversaturation is fairly high, crystallization without selection may be expected.

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Crystallochemical investigations of isomorphism have now continued for almost two centuries, starting with the discovery of this phenomenon by E. Mitscherlich in 1819. The constitution and properties can be satisfactorily explained for compounds of variable composition, thanks largely to the profound achievement in the structural analysis of crystals. Conversely, the crystal genetic aspect of isomorphism has come to the limelight only quite recently, starting in the mid-20th century, and progress in this field is much more modest due to the complexity of the crystal–medium systems and the absence of a standardized methodological basis (Glikin, 1995a, 1995b).

For example, thermodynamic studies of cocrystallization made it possible to develop an equation for the approximate evaluation of the partition coefficients for a system close to ideal, with certain equilibrium conditions and some other assumptions (see reviews in Urusov, 1971; Urusov et al., 1997). Although the theoretical and experimental data were sometimes proven to be highly consistent, the proposed approaches can hardly be considered universal.

The morphological–kinetic study of the growth of mixed crystals have revealed certain important effects:

the systematic variations in the partition coefficient for isomorphic components with an increasing oversaturation of some Tutton salts (Zhmurova et al., 1962; Zhmurova and Khaimov-Mal'kov, 1970a, 1970b); unusual overgrowths on the crystal faces of some low-soluble sulfates, carbonates, and chromates (Melikhov and Merkulova, 1975; Prieto et al., 1997); the growth of epitaxial islands during the simultaneous dissolution of adjacent areas on the faces of semiconductor crystals of the $A^{III}B^V$ type (Bolkhovityanov, 1981, 1990); and the deceleration of the growth of mixed crystals compared to the growth of pure compounds in the $K_2(S,Cr)O_4$ series (Kasatkin et al., 1995).

These phenomena were interpreted within the scope of classic concepts of the growth of crystals of invariable composition by means of the incorporation of particles into growth sites (indents) in growth steps. The selection of components at a low oversaturation was regarded as a statistical process coupled with the subsequent diffusion-controlled equalization of the crystal composition. For high degrees of oversaturation, a mechanism of “selection-free” crystallization was proposed (Chernov, 1980). It was thought that the selection process was controlled by deformations in the crystal lattice around a newly incorporated particle (Iiyama, 1974, quoted from Urusov, 1997). The deceleration of

the growth of mixed compounds and their local dissolution was believed to be accounted for by differences in the unit cell parameters (heterometry) of the matrix crystal and an overgrowing layer, with these differences inducing inconsistency defects and an increase in the potential at the growth front of a step (Melikhov and Merkulova, 1975; Bolkhovityanov, 1981, 1990; Kasatkin et al., 1995).

The aforementioned and other traditional interpretations of the genesis of mixed crystals failed, however, to settle the main problem of isomorphism, namely, the mechanism “employed” by the system to regulate the proportions of components in order to meet the condition of crystal growth. This publication proposes a solution to this problem on the basis of our concept of a specific genetic nature of isomorphic–mixed crystals. The unusual character of their growth was first noted and interpreted for the isothermal process of isomorphic metasomatic replacement (Glikin and Sinai, 1983), after which we extended our research to the complex of the growth and replacement processes and phenomena that are characteristic of mixed crystals and untypical of crystals of a constant composition (Glikin, 1995b, 1996; Kryuchkova et al., 2002; Glikin et al., 2003; Glikin and Sinai, 2004; Voloshin et al., 2004; Woensdregt and Glikin, 2005; Franke et al., 2006). The universalism of our conclusions was justified by the testing of numerous aqueous salt systems, observations of the phenomena listed above in high-temperature aqueous silicate experimental systems and samples of naturally occurring rocks, and the validation of the theory by basic physicochemical and crystal genetic principles. The experimental data and conceptual basis were systematized in the monograph (Glikin, 2004).

The most remarkable feature of the origin of mixed crystals is the fact that the most important role in this process is played by the exchange reaction between the crystal and solution. This reaction uniquely corresponds to the metasomatic replacement of the crystal in saturated solutions under isothermal–isobaric conditions and accompanies the growth and dissolution in over- and undersaturated solutions, respectively. The replacement proceeds via interrelated elementary acts of the dissolution of the matrix crystal and the autoepitaxial growth of a newly formed layer, with both processes occurring simultaneously at numerous sites at the crystal surface that randomly alternate at this surface and are displaced along it. Autoepitaxy ensures the inheritance of the primary single-crystalline integrity of the growing crystal. Therefore, the crystal either incorporates inclusions that compensate the deficit in the newly formed material or overgrowths develop on the crystal to counterbalance the excess of the newly formed material.

The physicochemical aspect of replacement is that the compositions of the solid and liquid phases shift from their starting values until a thermodynamic equilibrium is reached. Thus, the “foreignness” of the solu-

tion with respect to the crystal induces the dissolution of the latter, which, in turn, leads to the oversaturation of the solution with respect to its “own” crystalline phase and the precipitation of the latter (the process of salting-out). In undercooled or overheated solutions, salting-out is combined with direct growth and dissolution processes. A particular state of the system is the heterogeneous metastable equilibrium of an undercooled solution with “foreign” crystals of different compositions from those in a thermodynamic equilibrium with this solution (when a solution is saturated with respect to a pair of isomorphic components, the metastable equilibrium may involve crystals of two isomorphic compositions). This metastable state develops because the dissolution of the crystal stops at a certain degree of undercooling, and this terminates the whole salting-out (replacement) reaction.

The results of our research provide a direct solution to the problem concerning the regulation of the crystal composition. The principles of the so-called assembly mechanism proposed for the selection of isomorphic components by a crystal in a proportion required by a given combination of conditions (composition of the solution, undercooling/overheating, and temperature) are as follows. (1) Diverse assemblages of particles settling onto the surface are characterized by a certain statistical distribution according to their composition. (2) Only those assemblages can survive, whose compositions are consistent with the above-listed conditions. (3) All other assemblages dissolve and, thus, initiate the salting-out of the surviving assemblages.

The results of some of our experiments on the epitaxial growth of particles on an isomorphic matrix and the homogeneous spontaneous precipitation of crystals validate the proposed model. The briefness of the experiments (which lasted for 10–15 s) led us to conclude that the obtained compositional and size distributions of the crystals are close to the snapshot of the current state of the system.

Figure 1 presents an example of the development of assembly-type $(K,Rb)HC_8H_4O_4$ texture in an etching pit on the cleavage plane of a $KHC_8H_4O_4$ crystal that interacted with a saturated $RbHC_8H_4O_4$ solution at room temperature. The image was obtained on a Park CP atomic force microscope in a dry state, after the interaction of the plane with a solution droplet that was placed onto this plane and then removed after 10 s by compressed air (Woensdregt and Glikin, 2005). It is reasonable to suggest that the process was a combination of isomorphic substitution and growth maintained by the evaporation of the droplet.

The flat area in the lower part of Fig. 1 is the bottom of the pit, and the rest of the image corresponds to its slopes, which show dissolution steps slightly less than 13 Å high, i.e., corresponding to the d-spacing. The steps include protuberances ranging from ~70 nm to ~1 μm in size. These protuberances developed because the dissolving steps locally grew at some sites. The

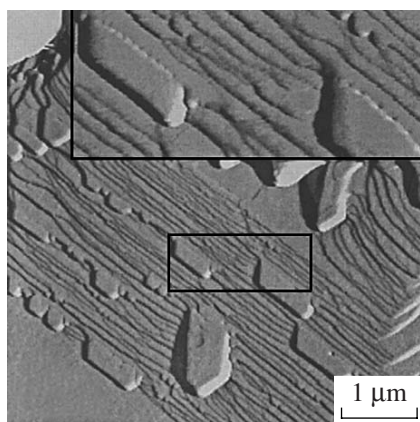


Fig. 1. Growth assemblies (protuberances) of (K,Rb)HC₈H₄O₄ in an etching pit on a crystal of KHC₈H₄O₄ during the initial stage of its interaction with a RbHC₈H₄O₄ solution.

interdependence of the dissolution and growth processes follows from the fact that the steps are curved in the vicinity of the protuberances according to the acceleration of the dissolution process. Note that the protuberances originate, according to the main concept (Glikin, 1996, 2004), via the expansion of existing steps, a process that does not require overcoming a significant activation barrier due to the necessity of two-dimensional nucleation or the development of new dislocation steps. At the same time, the compositions of the steps and protuberances are a priori different, which results in a difference in the unit-cell parameters and inconsistency defects. The magnified fragment in the inset in Fig. 1 clearly demonstrates that the boundary between a step and the protuberances is marked by the dislocation of the vacancy defects.

The protuberances should be regarded as spontaneously developing assemblages of isomorphic particles. It is important in the context of our discussion that the protuberances broadly vary in habit, degree of faceting, and size (for at least 1.5 orders of magnitude). The variations in their habit correspond to various compositions, as is evident from our experimental results (Glikin and Woensdregt, 2003; Glikin, 2004, pp. 143–144): the protuberances elongated along and across the terraces are enriched in K and Rb, respectively. The various extent of faceting demonstrates the differences in the resistance of the protuberances: those better faceted grow or are in equilibrium and retain their faceting, whereas rounded protuberances dissolve. The variation in the size of the protuberances displays their different growth rates: the larger ones grew under more favorable growth conditions, whereas the smaller ones were, conversely, formed under less favorable conditions. We identified the following tendencies consistent with our model. The stable (faceted) protuberances are large and prone to be K- and Rb-rich in the virtual absence of intermediate habit types and compositions. The unsta-

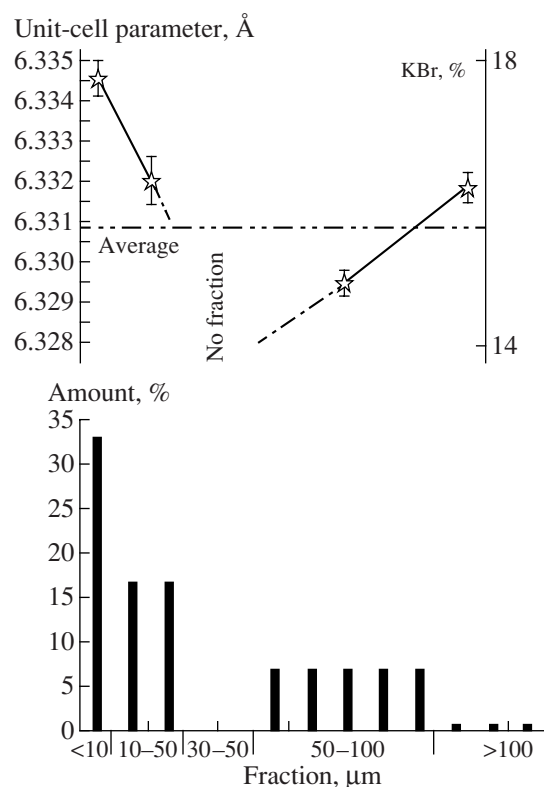


Fig. 2. Distribution of K(Cl,Br) single crystals according to their composition and size during an initial stage of the spontaneous precipitation from solution.

ble (rounded) protuberances are small and, as follows from their equant morphologies, have intermediate compositions.

The distribution of the spontaneously precipitating mixed crystals according to their isomorphic composition and size shows similar characteristics. Figure 2 exhibits the results of the K(Br,Cl)–H₂O precipitation from a solution with KCl/KBr (wt %) = 60/40, which was saturated at 20°C and then undercooled by 5°C.¹ The precipitation was carried out at active stirring, from a preliminarily undercooled solution, the solution was decanted after 15 s, and the sample was dried by filter paper. The compositional variations of the solution during the early stages of the process were generally insignificant. The sample was then screened through plastic sieves to separate it into the following size fractions: <10, 10–30, 30–50, 50–100, and >100 μm. The composition of the fractions was calculated from the unit-cell parameters (which were determined by X-ray powder diffraction), based on the available literature data on the linear Vegard dependence for this series (STOE diffractometer, Mo radiation, transmission regime within the

¹ The mass crystallization was studied for the systems K(Br,Cl)–H₂O and (Pb,Ba)(NO₃)₂–H₂O at Munich University. All of the results were reported at conferences (Glikin, 2006; Glikin et al., 2006a, 2006b) and will be published in a special paper.

range $2\theta = 5\text{--}46^\circ$; the parameters were determined accurate to $0.0003\text{--}0.0004$ Å).

Figure 2 exhibits the significant differences between the compositions of various size fractions: the fine- and coarse-grained fractions of $\text{K}(\text{Br},\text{Cl})$ are enriched in more soluble KBr compared to the medium-sized fractions.² The modal proportions of the fractions display a bimodal distribution with the complete absence of fractions $30\text{--}50$ μm . These results obviously resemble the data reported above for the surface process.

The mechanism proposed for the selection of the components during the growth of mixed crystals operates on a scale of large enough assemblages of particles through the survival of some assemblages and the dissolution of others. The model for this mechanism directly follows from our earlier concept of the growth of mixed crystals and is confirmed by experimental data on the interrelations between the stability of crystalline assemblages and their isomorphic composition, which are detected during both heterogeneous epitaxial processes on a crystal surface and homogeneous spontaneous nucleation. The details of these experimental data, such as the bimodal distribution of the crystals according to their composition and size, are beyond the scope of this publication. It is, however, pertinent to note that, previously, we predicted the compositional bimodality, proceeding from the physicochemical analysis, as a consequence of metastable heterogeneous equilibrium between the crystals and the undercooled solution. The existence of this phenomenon was then proven experimentally (Glikin, 1996; Kryuchkova et al., 2002; Glikin, 2004). The traditionally discussed statistical selection of individual ions seems to play a subordinate role, although it may become more significant at a rather low concentration of one of the isomorphic components, i.e., when the ideal conditions are approached. It is also reasonable to expect that the "selection-free" crystallization may take place at sufficiently high degrees of oversaturation, although our experimental data on the compositional bimodality of $\text{K}(\text{Br},\text{Cl})$ and $(\text{Pb},\text{Ba})(\text{NO}_3)_2$ crystals during undercooling by 20°C casts some doubt on the accessibility of the required extent of oversaturation.

In conclusion, it should be mentioned that the discussed concept of the genetic nature of isomorphism should be regarded as the basis in interpreting the genesis of minerals, for example, during thermobarometric and other reconstructions of natural conditions. Obviously, the development of the theory of isomorphism and the possibility of its application to studying crystalline materials and growing crystals may be most efficient only in the context of the combined crystallochemical and crystallogenic concepts and theories.

² Conversely, the fine- and coarse-grained fractions in the system $(\text{Pb},\text{Ba})(\text{NO}_3)_2\text{--H}_2\text{O}$ are enriched in less soluble $\text{Ba}(\text{NO}_3)_2$ compared to the medium-sized fractions.

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