ANALYSIS OF THE FORMATION OF GROWTH SECTOR ZONING IN MIXED CRYSTALS USING LINEAR THERMODYNAMICS OF IRREVERSIBLE PROCESSES

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It is well known that the impurity concentration in different growth pyramids of one and the same crystal can differ significantly even to the extent that the separate pyramids are built by different minerals (for instance, by the end members of isomorphous series [1]). The sector inhomogeneity of mixed crystals is often observed in both natural and artificial crystal growth systems. The mechanisms of its formation are treated in different ways, but in most cases, either as the effect of growth rate or surface effect, or both [2]. The existing models are based on the preferable uptake (adsorption) of impurity by the crystal faces of the particular type, and the interplay between the growth rate of the crystal and the diffusivity of admixed element in near-surface region [3]. The growth rate of the crystal face in such models determines only the possibility of conservation of inhomogeneity created by the selective surface enrichment of the crystal face. It remains unclear whether different growth rates of non-equivalent faces can directly generate the sector inhomogeneity.

Using the principles of linear irreversible thermodynamics, the following kinetic equations were obtained for normal movement of the faces of two coexisting mixed crystals:

$$\frac{\mathbf{dh_i'}}{\mathbf{dt}} = -\frac{\mathbf{V}_{01}\mathbf{X_i'} + \mathbf{V}_{02}(1-\mathbf{X_i'})}{\mathbf{TX_i'}}\mathbf{L_i'}\left[\mu_1^0 - \mu_2^0 + \mathbf{RT}\ln\frac{\mathbf{X_i'}}{1-\mathbf{X_i'}} + \mathbf{Q}(1-2\mathbf{X_i'}) - \frac{\partial \mathbf{g_L}}{\partial \mathbf{X_L}}\right];$$

$$\frac{\mathbf{dh_i''}}{\mathbf{dt}} = -\frac{\mathbf{V}_{01}\mathbf{X_i''} + \mathbf{V}_{02}(1-\mathbf{X_i''})}{\mathbf{TX_i''}}\mathbf{L_i''}\left[\mu_1^0 - \mu_2^0 + \mathbf{RT}\ln\frac{\mathbf{X_i''}}{1-\mathbf{X_i''}} + \mathbf{Q}(1-2\mathbf{X_i''}) - \frac{\partial \mathbf{g_L}}{\partial \mathbf{X_L}}\right],$$

where μ_1^0 and μ_2^0 are the chemical potentials of pure components, X_i' and X_i'' the mole fractions of the component i in the growth pyramids of coexisting solid solutions α' and α" , L_i' and L_i'' the Onsager kinetic coefficients for i-th face, g_L and X_L the molar Gibbs energy and the mole fraction of the component i in the growth medium, correspondingly, V_{01} and V_{02} the molar volumes of pure components.

Further let us consider the case when one side of the immiscibility curve coincides with the corresponding section of the equilibrium solvus that is formally mean that the growth rate of the crystal of this phase is equal to zero. Really, the growth rate is not equal to zero, but we can examine some face i of the phase α", which growth rate is very close to zero and so, is represented in the crystal shape of the particular equilibrium phase. Therefore, for such virtual face the equilibrium condition is satisfied: $\frac{\partial g_L}{\partial X_L} = \frac{\partial g_0}{\partial X_0}$, where X_0 corresponds to equilibrium solvus curve. Then instead of $\frac{\partial g_L}{\partial X_L}$ we substitute its value $\mu_1^0 - \mu_2^0 + RT\ln\frac{X_0}{1-X_0} + Q(1-2X_0)$ and the above mentioned equations are simplified.

Using the numerical example of the system ZnS-HgS (Fig.) it is shown that in contrast to the postulate accepted in most models, the different growth rates of the faces can directly generate the inhomogeneities of the growth pyramids of crystallographically nonequivalent faces but not only facilitate the retention of impurity distribution provided by different adsorption abilities of the faces. The reason is as following. If in equilibrium conditions the coefficients of co-crystallization of isomorphous components depend on solubility of pure components and thermodynamic functions of their solid state mixing, under the growth conditions they still depend on the relations of supersaturations in components, not equal for faces grown with different rates.

The consequences for experimental geochemistry connected with the kinetic diagrams are considered. In principle, such diagrams allow to solve the reciprocal task – to determine the growth rates of natural crystal faces, corresponding to observed extent of sector chemical zoning. The solid solutions of many mineral systems are decomposed in the region of low temperatures, where *in situ* equilibrium cannot be attained for reasonable time. Dealing with the set of kinetic diagrams, one can obtain the immiscibility curves close to equilibrium binodals.

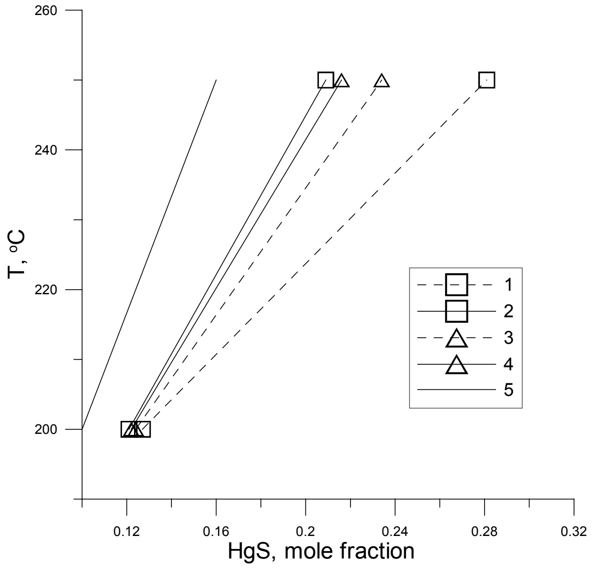

Fig. Composition of growth pyramids of mixed crystals (Zn,Hg)S at the sphalerite section of binodal as a function of the face growth rate.
1,2 – {100}, 2x10^{-10} and 1x10^{-10} m/s, correspondingly; 3,4 – {111}, 8x10^{-11} and 6x10^{-11} m/s, correspondingly; 5 – the section of equilibrium solvus (calculated).

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