MORPHOLOGICAL STABILITY OF $M_{1-x}R_xF_{2+x}$ SOLID SOLUTION SINGLE CRYSTALS (M – ALKALINE EARTH, R – RARE EARTH ELEMENTS)

P.P. FEDOROV, T.M. TURKINA, B.P. SOBOLEV

Institute of Crystallography, USSR Acad. Sci., Moscow, USSR

Growing of good quality single crystals of the fluorite-type, $M_{1-x}R_xF_{2+x}$ concentrated solid solutions (M – alkaline earth, R – rare earth elements) is restricted by the formation of cellular or dendritic substructure into melt-grown crystals (figure 1) [1-4]. It is an example of dissipative semi-ordered structure which arises as a result of self-organization of the system liquid-solid during crystallization.

Different areas of crystal body differ from one another in the concentration of the components in the solid solution. Since the refractive index of solid solutions strongly varies with concentration (figure 2), variations of the chemical composition lead to a specific optical picture (figure 1). Crystals with a cellular substructure do not transmit the image and they cannot be applied in optics. Besides, such crystals are not suitable for crystal structure determinations, and, in many cases, for the determination of their physical properties.

The cellular substructure is a result of loss of stability of the flat crystal-melt interface due to concentration (or constitutional) supercooling during crystallization of solid solutions [5-7]. A scheme of this process (one-dimensional directed crystallization of a binary alloy) is shown in figure 3. Since the distribution coefficient $k = C_S/C_L$ differs from unity (which is a common case for solid solutions) a jump of the concentration is observed at the interface. If k exceeds unity, a low concentration region forms in front of the interface. If k is less than unity, a region with a higher concentration arises there. The situation is smoothed by ion diffusion in melt, thus, in the case of k exceeding unity, the concentration C in the melt increases with moving from the interface. As C is connected with the crystallization temperature, this relation is expressed as the phase diagram, the equilibrium freezing temperature rises near the interface. This is true for $k < 1$, too. If the system crystal-melt lies in the thermal field with insufficient temperatu-
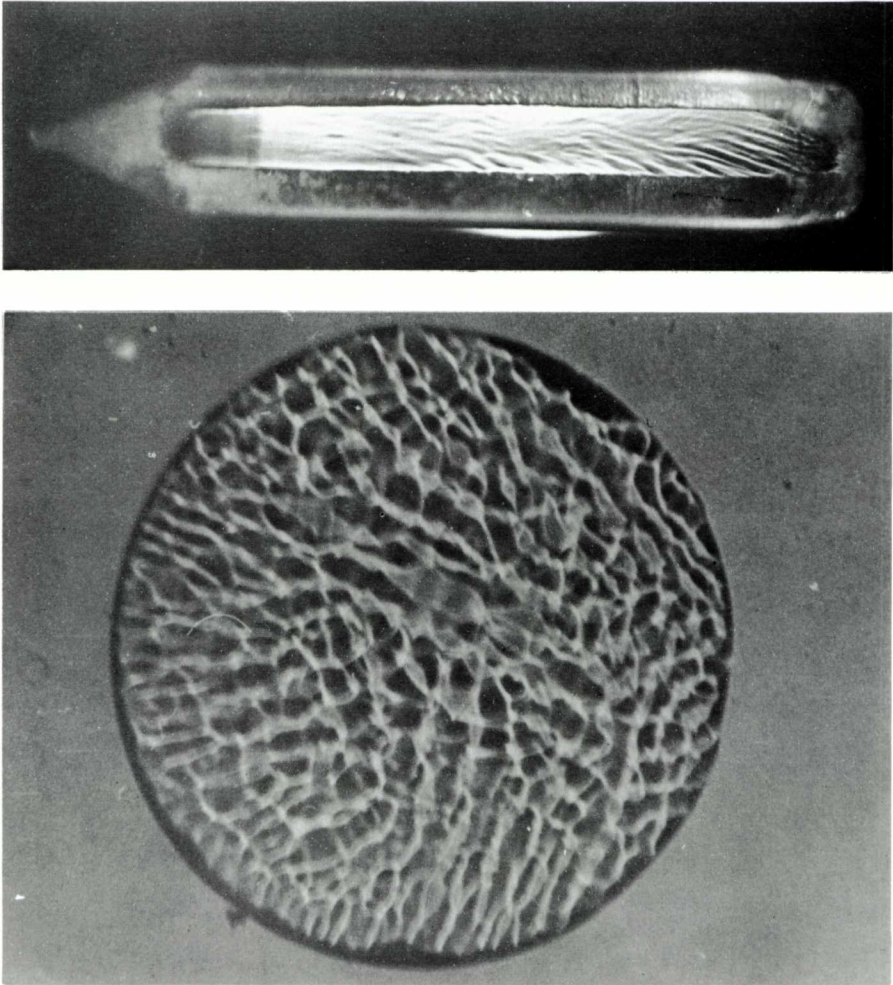
Fig. 1. Picture of optical heterogeneity typical of $M_{1-x}R_xF_{2+x}$ single crystals grown by the Bridgman technique. Crystal diameter is 7 mm, crystal length is from 40 to 50 mm.
a. $Sr_{0.9}La_{0.1}F_{2.1}$; R = 3.6 mm/h.
b. $Sr_{0.93}La_{0.07}F_{2.07}$; R = 9.6 mm/h, water thickness is 1 mm.

re gradient G, an extrasupercooled region is formed ahead the crystallization front. In this case small hill-like fluctuations on the surface should develop into the melt and the flat interface becomes unstable.

This supercooling fails to take place if the temperature gradient G in the melt near the crystallization front is greater than the gradient of the
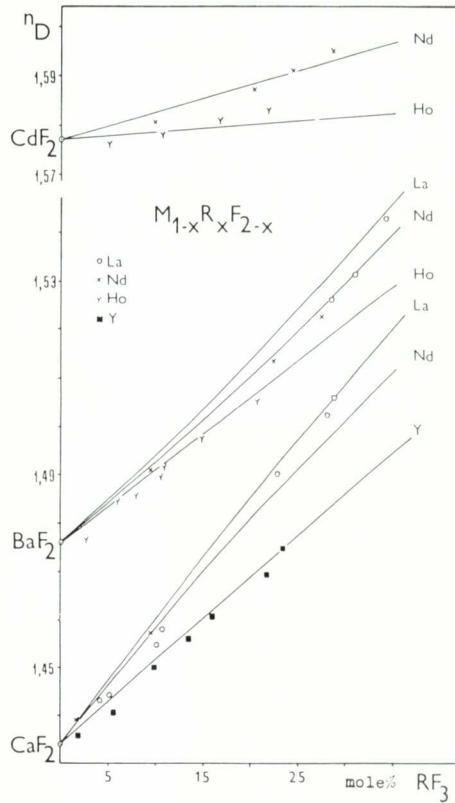
Fig. 2. Variations of refractive index of $M_{1-x}R_xF_{2+x}$ solid solutions with concentration.

equilibrium crystallization temperature T_L, determined by the phase diagram liquidus curve:

$$G = \left.\frac{dT}{dx}\right|_{x=0} > \frac{dT_L}{dx}, \tag{1}$$

where x is the ingot length.

Let us write down the equation for the material balance at the crystallization front:

$$R \triangle C = -D \frac{dC}{dx} \tag{2}$$

where R is the growth rate, D is the interdiffusion coefficient, $\triangle C$ is the abrupt change of the concentration at the interface.

Taking into account the fact that

$$\frac{dT_L}{dx} = \frac{dT_L}{dC} \cdot \frac{dC}{dx} = m\frac{dC}{dx} \tag{3}$$

where m is the liquidus curve tangent, we obtain

$$\frac{GD}{R} > m\triangle C = F(C) \tag{4}$$

as the stability criterion.

The criterion (4) is equivalent to the well-known Tiller criterion [6, 7] which was introduced for the stationary crystallization process without stir-
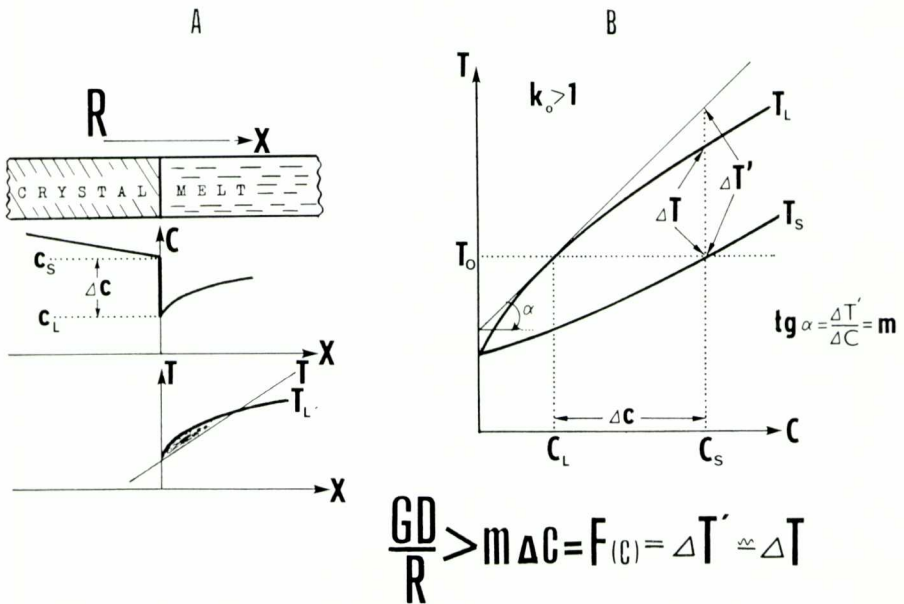

$$\frac{GD}{R} > m\,\Delta C = F_{(C)} = \Delta T' \cong \Delta T$$

Fig. 3. Scheme of the concentration supercooling near the solid-liquid interface during unidirected crystallization of a two-component ingot (A) and scheme of calculation of stability function from a phase diagram (B).

R is the crystallization rate; C is the concentration, T is the temperature, x is the length, $k = C_S/C_L$ is the distribution coefficient, D is the diffusion coefficient, G is the temperature gradient.

ring in the melt with a low impurity content ($c \ll 1$; k and m being constants). The same limitations were used in the majority of works on morphological stability [5-19]. However, expression (4) is suitable for concentrated solid solutions, which are interesting, particularly, in MF_2-RF_3 systems.

The right-hand part of inequality (4) was called the planar front stability function [1, 2]. If the crystallization process takes place under near-equilibrium conditions (distribution coefficient k may be assumed to be equal to the equilibrium value), the stability function can be calculated from the phase diagram (figure 3), as follows:

$$F(C) = \triangle T' \simeq \triangle T \tag{5}$$

Hence, the morphological stability of the flat interface is roughly determined by the difference between the liquidus and solidus curves for the composition, which corresponds to the solid state phase concentration at the crystal-melt interface.

The stability function has the temperature dimension. This function is non-negative and turns to zero for the pure components and extrema points on the solid solutions melting curves ($\triangle C = 0$).

Figures 4, 5 present some examples showing the relationship of F(C) for various types of phase diagrams: continuous solid solution without extrema (figure 4a), continuous solid solution with the minimum (figure 4b), solid solution with the maximum (figure 5a).

The physical meaning of the stability function is as follows: if the figurative point corresponding to the real crystallization process which is characterized by the values of D, R, G, lies under the stability function, the concentration supercooling takes place.

Two particular cases are important.

At low impurity concentrations F(C) actually is a straight line originating from the coordinate zero according to the Tiller approximation. For the maximum and minimum points, where the solidus and liquidus curves merge and have a common horizontal tangent line (as follows from the Van der Waals equation for the coexistent phases in the binary systems [22]) $\triangle C = 0$ and m = 0. Hence, at extrema points F(C) = 0 and dF(C)/dC = 0.

Thus, the compositions of extrema points on the melting curves are very convenient for growth of high-quality crystals from melt (fig. 6), as the flat crystal-melt interface is stable at any values of R and G and small deviations of the composition do not lead to loss of stability of the interface. At such points we have an original case-stability of stability.

The maxima on the solid solutions melting curves are typical of the MF_2-RF_3 systems as a result of heterovalent substitutions [23-25]. The sta-

bility functions, calculated from phase diagrams for 42 $M_{1-x}R_xF_{2+x}$ fluorite-type solid solutions were published in [1].

In order to regulate the conditions (R, G) of crystal growth for the preparing of high-quality crystals and to compare directly the stability curves calculated from phase diagrams versus the experimental data, the diffusion coefficient D values are needed for various elements and various compositions of the melt. But D values are usually unknown, and the procedure of measurement is very complicated. Still, a possibility exists of solving an inverse problem, namely: estimation of values D based on the experimental data using the concentration series method when under the same conditions
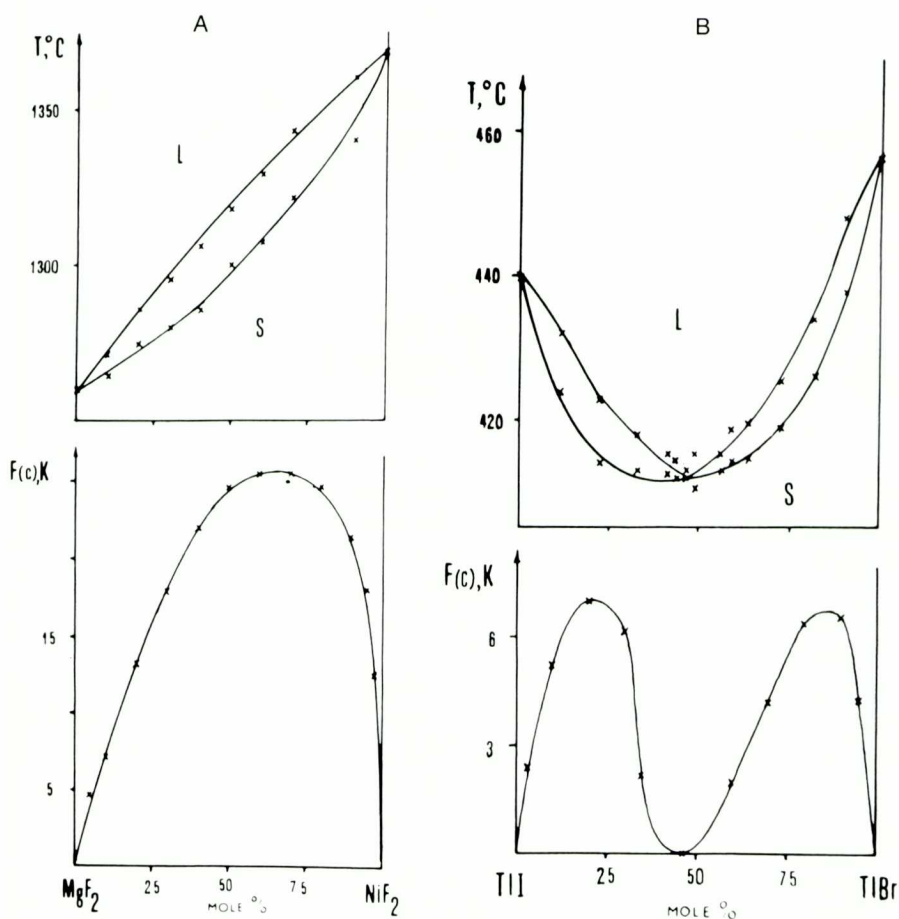

Fig. 4. Typical phase diagrams and corresponding stability function
A) System MgF_2-NiF_2 according to [20]
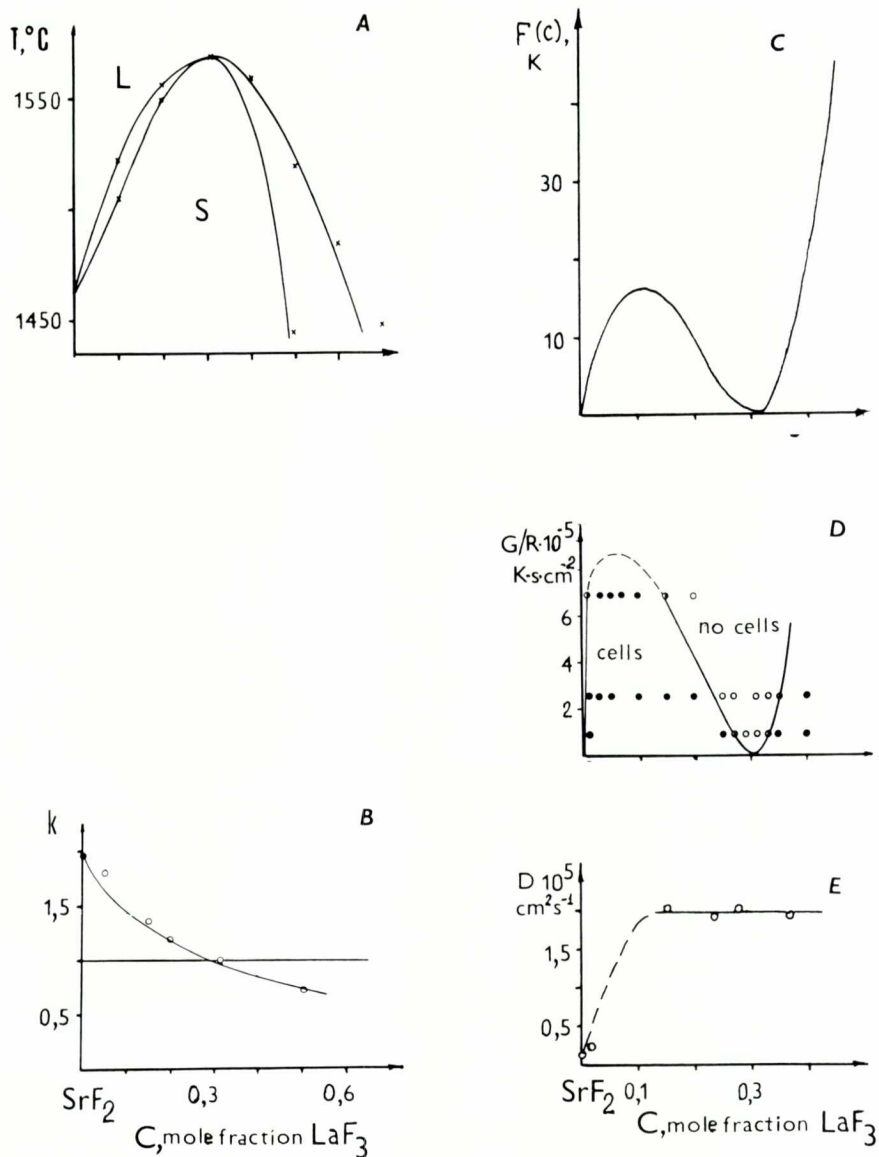B) System TlCl-TlBr according to [21]

Fig. 5. Cell formation in the SrF_2-LaF_3 system (C is the mole fraction of LaF_3)
A: solidus and liquidus curves for $Sr_{1-x}La_xF_{2+x}$ solid solution.
B: concentration dependence of the distribution coefficient k.
C: calculated stability function.
D: experimental areas of a flat interface instability, black circles are crystals with cells, light circles are crystals without cells.
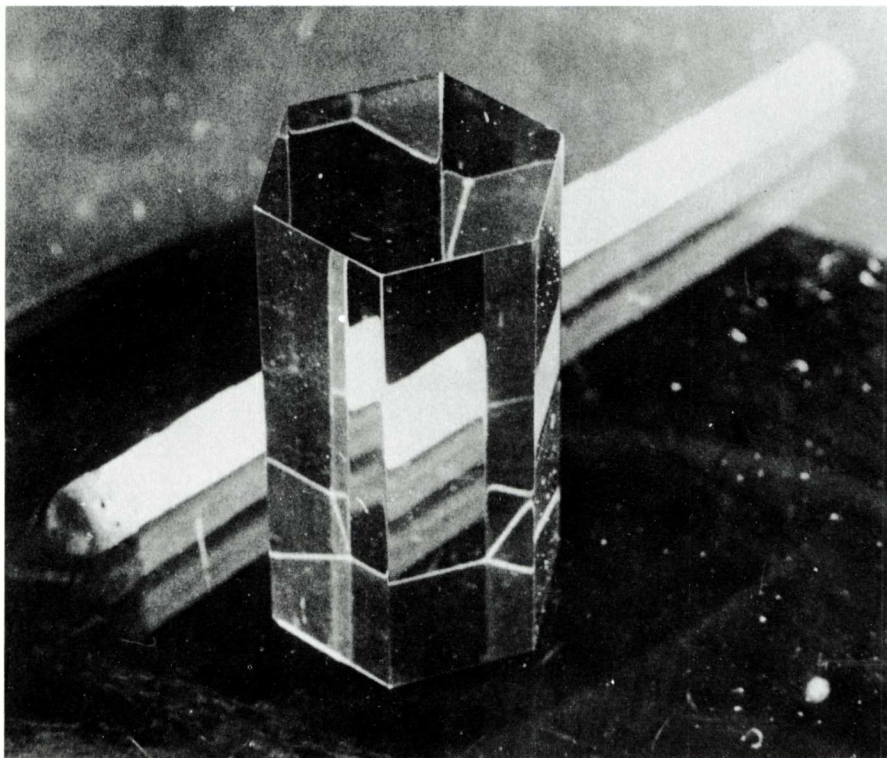E: concentration dependence of the diffusion coefficient in the melt.

Fig. 6. Single crystal of $Sr_{0.69}La_{0.31}F_{2.31}$ congruent melting composition (1570°C): most refractory inorganic fluoride.

(R and G being equal) several crystals are grown simultaneously. The optical inhomogeneity of the grown crystal serves for the detection of those critical concentrations when cells appear and disappear.

Figure 5d shows the results of experiments for $Sr_{1-x}La_xF_{2+x}$ solid solutions. Graphite crucibles with 7 channels were used for the Bridgman method crystal growth. Crystallization rate was 3.6, 9.6 and 25.4mm/h, temperature gradient – 70°/cm. The values of D (figure 5e) were calculated by comparing figures 5d and 5c.

Figure 7a shows the values of D, calculated in such a way for different combinations of M^{2+} and R^{3+} cations in concentrated $M_{1-x}R_xF_{2+x}$ melts. In figure 7b the average values of D for CaF_2, SrF_2 and BaF_2-based solutions are presented. It is interesting that the values of D for CaF_2 series are approximately one order larger than those for BaF_2 series. It means that the growth of high quality single crystals of $Ca_{1-x}R_xF_{2+x}$ solid solutions is much easier than the growth of BaF_2-based ones.
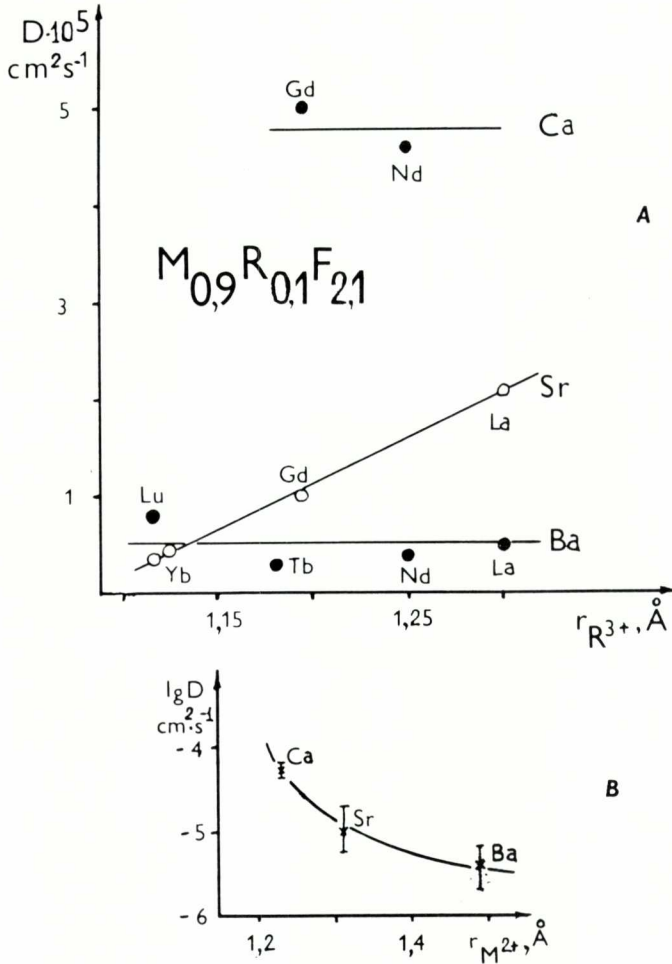
Fig. 7. Variations of diffusion coefficients of cations in the $M_{1-x}R_xF_{2+x}$ melt with the ionic radii of R^{3+} (A) and M^{2+} (B), average values.

The abnormal dependende of diffusion coefficient on the ionic radii of trivalent cations (the increase of D with the increase of cationic size) for SrF_2 series can result from cluster formation in the melt. It is indirect evidence that rare earth cations aggregate not only in crystals but in melts, too, as it was suggested in [26]. Indeed, results of the study of defect structure of $M_{1-x}R_xF_{2+x}$ solid solutions testify to the existence of small R_4F_{23} clusters in solid solutions with large rare earth cations (R = La – Nd) and larger R_6F_{36-37} clusters for solid solutions with small rare earth cations [27].

Figure 8 shows relations between the melting curves of the solid solution, stability function, the time which is necessary to produce good quality crystals of fixed sizes and, on the other hand, the size of high quality crystals which will be grown from melt within a fixed time.

The method suggested in this paper illustrated by fluorite-type solid solutions is based upon some suppositions, analyzed in [1, 2]. Apparently, it can be extended to solid solutions of some other types, with the normal mechanism of crystallization from melt. Many organic substances having low melting entropy satisfy this condition.
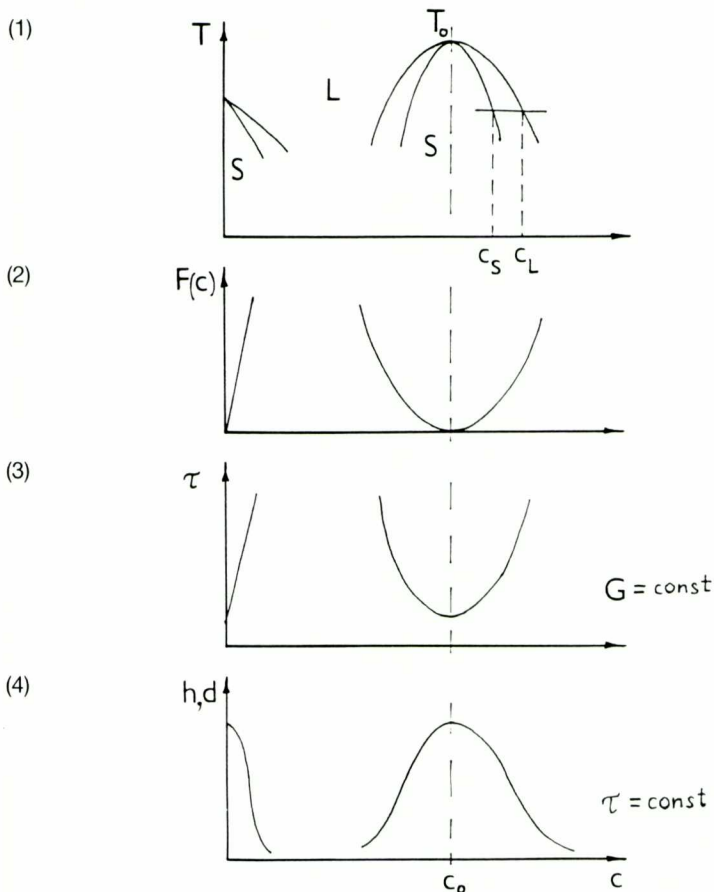

Fig. 8. Relations of the character of melting of solid solutions (1) with the stability function of flat interface (2), required time τ for growth of perfect crystals (3) and their available sizes (h, d) (4). T is the temperature, C is the concentration, G is the temperature gradient, L is the melt, S is the solid phase.

ABSTRACT

Stability conditions for a plane crystallization front of fluorite grossly nonstoichiometric phases $M_{1-x}R_xF_{2+x}$ (M = alkaline earth, R = rare earth elements) from two-component melts have been considered. We found a dependence of the formation of a cellular substructure in crystals on the growth conditions and dopant diffusion coefficient. The regions near extrema (maxima) on the liquidus curves of fluorite phases are more favourable for preparation of homogeneous single crystals than regions with low contents of the second component.

The dopant diffusion coefficients in the melt have been estimated on the basis of the criterion of plane front stability, as well as experiments on growing crystals under various conditions and data on melting diagrams for MF_2-RF_3 systems. Diffusion coefficients of the CaF_2 series of solid solutions exceed those of the BaF_2 series by one order of magnitude. The anomalous dependence of R^{3+} diffusion coefficients on their ionic radii for the SrF_2 series is accounted for by differences in sizes of clusters containing R^{3+} of the beginning and the end of the rare earth family.

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