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Kinetics of barium molybdate crystallization from lithium chloride melts

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The kinetics of crystal growth of barium molybdate from unstirred supersaturated solutions of molten lithium chloride has been studied at 700 and 800° C. The growth is shown to be controlled by the rate of diffusion up to an extent of 35% and 56% at the two temperatures. At first the growth occurs characteristically by slow diffusion transport of the solute through the solution on to the crystal surface and later by a surface-reaction controlled mechanism.

1. Introduction

Several workers [1–5] have reviewed the crystallization of inorganic materials from high-temperature solutions. Alkaline-earth metal molybdates and tungstates have been prepared by crystallization from lithium chloride and sodium molybdate/tungstate melts [6–12]. Packter and Roy [12–16] reported their studies on the growth kinetics of these crystals. Packter [17] has also carried out studies of precipitation of certain metal molybdates from aqueous solutions over a certain range of metal salt concentrations. Hitherto, only some preliminary work has been reported on the kinetics of crystal growth of barium molybdate from LiCl melts.

We present here some further investigations of the kinetics of crystallization of barium molybdate from unstirred supersaturated solutions of lithium chloride melts at 700 and 800° C. The mechanism of production of large step-height spirals on $BaMoO_4$ in different morphology by the flux evaporation method has been suggested elsewhere [18].

2. Experimental procedure

2.1. Materials

The chemicals used were "Sendez Swijur" $BaMoO_4$ powder of 99.6% purity and "chemapol" LiCl of 99% purity.

2.2. Solubility

The solubility of $BaMoO_4$ in LiCl melts in the range 650 to 850° C was determined by the supersaturation method. A weighed amount of LiCl powder was melted in a platinum crucible in a vertical tube muffle furnace which was capable of giving a temperature of about 1000° C. Constant temperature was maintained through a variable voltage transformer and measured using a Pt–Pt/10% Rh thermocouple. Then, an increasing amount of barium molybdate powder was added to the molten solvent until a saturated solution was attained. The solution was considered to be saturated when traces of the excess solute deposited at the bottom of the crucible. The weight of the solute thus dissolved was noted, and the solubility (g/g solution) determined.

2.3. Crystallization and characterization

Using the solubility curve, the appropriate amounts of barium molybdate and lithium chloride were placed in a 25 ml platinum crucible which was covered with a loosely fitting lid to prevent excessive evaporation. Since LiCl evaporates much faster above 700° C, the evaporation rate being $0.03\,\mathrm{g\,h^{-1}}$ at 800° C, for instance, the necessity of loosely covering the crucible was felt. It may be of interest to note that since the evaporation rate, which obviously has a bearing on crystallization rate, depended on temperature and not time, the kinetics were studied at different temperatures. The saturated solutions were prepared at temperatures of T_i, given by

$$T_\mathrm{i} = T_0 + \Delta T,$$

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where T_0 is the temperature planned to study the crystallization, and $\Delta T = 50°$ C. The melt was soaked at the higher temperature T_i for about 30 min. Then the furnace was cooled rapidly to the crystallization temperature, T_0, and held there for the required duration, which is the time allowed at T_0 for evaporation, to initiate free crystallization from the unstirred solution. This duration was chosen arbitrarily as 4 to 18 h in which the crystallization kinetics were investigated. After completion of this period the crucible was suddenly withdrawn from the furnace and the solidified melt dispersed and washed in distilled water until the extract was chloride free.

The crystallization was studied at 700 and 800° C and the crystals so obtained were characterized by X-ray diffraction and density measurements.

3. Observations and discussion

The solubility of barium molybdate in lithium chloride melt at different temperatures is shown in Fig. 1. The observed gradual increase in solubility is quite favourable for crystal growth to take place. The growth charge was heated at $\Delta T = 50°$ C above T_0, with a view to ensuring the removal of any undissolved excess nuclei which might have formed at T_0, failure to carry this out usually resulted in considerable spurious nucleation. The crystals obtained were tetragonal bipyramids having well-developed (0 1 1) faces. The average crystal lengths, l_t, at different growth times were measured using a travelling microscope. The l_t (cm) against t (h) plot so obtained is shown in Fig. 2. It is observed that the higher the growth temperature, the larger the growth rate, as expected. Furthermore, the crystal length increases regularly with the time allowed for evaporation.

After about 15 h evaporation, the crystal growth was found too slow to produce a measurable increase in crystal size, thereby generating the final, almost consistent, size l_f. Contrary to the theoretical approach, it is probable that the limiting growth rate is imposed by surface-kinetic processes such as desolvation, integration at kinks and removal of solvent molecules from the surface. In several cases spontaneous nucleation of further cyrstals as well might limit the experimental, maximum feasible, growth rate [1].

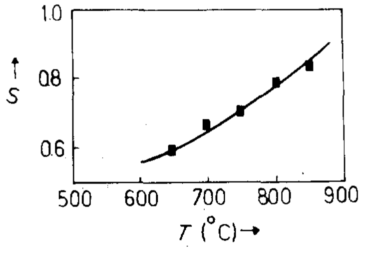

Figure 1 Solubility of BaMoO$_4$ in LiCl at different temperatures (S = g/g solution).

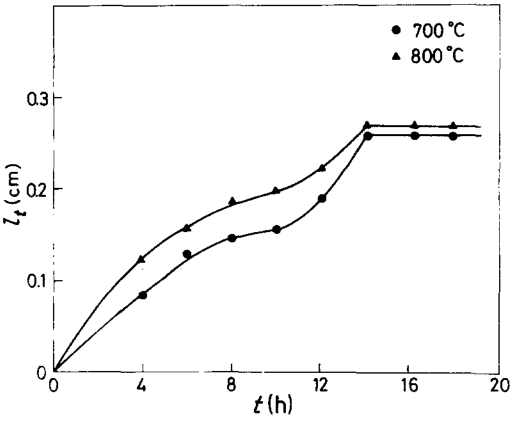

Figure 2 Plot of average crystal length against growth times at 700 and 800° C.

Since l_t is a function of growth time, it is worthwhile to study the degree of crystallization, α_t, which is measured by the ratio of the amount of substance crystallized to the amount able to crystallize, as defined by Nielsen [19] in the form;

$$\alpha_t = \frac{C_0 - C}{C_0 - S}, \qquad (1)$$

where C_0 is the initial concentration of the substance, C is the instantaneous concentration and S is its solubility. Equation 1 can be rewritten as

$$\alpha_t = \frac{l_t^3}{l_f^3} \qquad (2)$$

Thus, the variation in the degree of crystallization, α_t, with growth time, t, was computed, which is shown by continuous lines in Figs 3 and 4. The linear nature is indicative of uniform crystallization within the observed period. In the present case, the growth of BaMoO$_4$ by isothermal crystallization from unstirred LiCl solutions having low permeability, results from the flow of nutrient through the inter-particle void space to the reacting surfaces. Consequently, growth is believed to be controlled by the rate of diffusion of nutrient on to different growth faces [19]. The rate of growth of the larger side of the pyramid-shaped crystal, under consideration, as influenced by

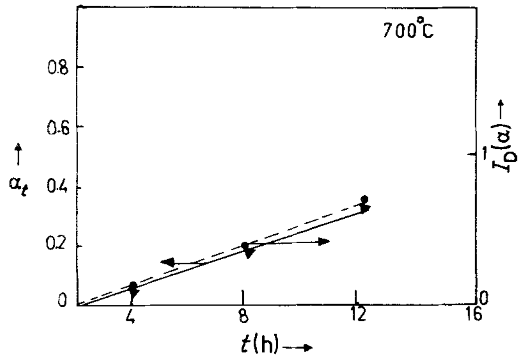

Figure 3 Degree of crystallization at different times for 700° C.

transport-controlled conditions at any time, can be expressed by the formula [19–21],

$$\frac{\mathrm{d}l}{\mathrm{d}t} = \frac{2\mathrm{Sh}\,\phi(\epsilon) D \Delta C_t}{l_t} \frac{\rho_\mathrm{S}}{\rho_\mathrm{C}} \ \mathrm{cm}^2\,\mathrm{sec}^{-1}, \tag{3}$$

or,

$$\frac{\mathrm{d}l}{\mathrm{d}t} = \frac{2K_{\mathrm{D_l}} \Delta C_t}{l_t} \ \mathrm{cm}^2\,\mathrm{sec}^{-1}, \tag{4}$$

where Sh is the dimensionless Sherwood number, $\phi(\epsilon)$ is an overall shape factor, D is the diffusion coefficient, ΔC_t is the excess solute concentration at any time, expressed in g/g solution and ρ_S and ρ_C are the solution and crystal densities, respectively.

The natural convection being very poor in the present case, Sh $\simeq 2$, as also conceived by Treybal [21]. A general solution of Equation 3, as arrived at by Nielson [19], is

$$I_D(\alpha) = \int_0^\infty \frac{\mathrm{d}\alpha}{\alpha^{1/3}(1-\alpha)} = \frac{1}{K_D} t. \tag{5}$$

The rate constant, K_D, having the dimension of time, contains all physical constants of the process including $K_{\mathrm{D_l}}$, ΔC_0, l_f^2 and t. Furthermore, $I_\mathrm{D}(\alpha)$ is to be regarded as the dimensionless time, or "chronomal", which is a characteristic parameter for diffusion-controlled and polynuclear-layer-controlled growth mechanisms. The significance of $I_\mathrm{D}(\alpha)$ is that if the size of a particle is known at a certain time, one can calculate at constant concentration the time at which it started with zero size. The integral in Equation 5 is solved, using standard methods [22], to give

$$I_\mathrm{D}(\alpha) = \tfrac{1}{2} \ln \frac{1-\alpha}{(1-\alpha^{1/3})^3} - 3^{\frac{1}{2}} \tan^{-1} \frac{3^{1/2}}{1+2\alpha^{-1/3}}. \tag{6}$$

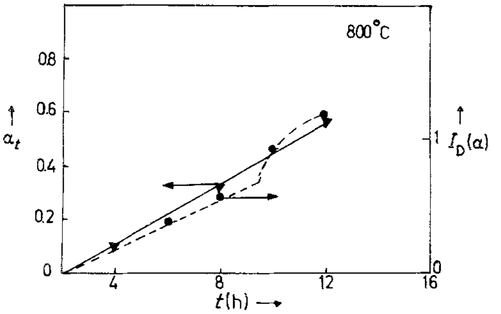

Figure 4 Degree of crystallization at different times for 800° C.

The kinetics of crystal growth in our experiments are checked by plotting the diffusion chronomal $I_\mathrm{D}(\alpha)$ against t. The necessary $I_\mathrm{D}(\alpha)$ values are, however, taken directly from Nielsen's table [19]. The plot is shown by dashed lines in Figs. 3 and 4. Clearly, the two plots are linear up to $\alpha_t \simeq 0.35$ for 700° C, and up to $\alpha_t \simeq 0.56$ for 800° C, respectively.

One may find it interesting to know the diffusion rate constant, $K_{\mathrm{D_l}}$, values. These have been evaluated from the slope of the linear part of $I_\mathrm{D}(\alpha)$ against t plots, using the relation,

$$K_{\mathrm{D_l}} = \frac{\mathrm{Grad}\ [I_\mathrm{D}(\alpha) \text{ against } t \text{ plot}]\ l_\mathrm{f}^2}{12\Delta C_0} \ \mathrm{cm}^2\,\mathrm{sec}^{-1}. \tag{7}$$

The respective ΔC_0 values are obtained from Fig. 1 and the results are collected in Table I.

In order that a crystal may grow from solution, the solute must be transported through the solution up to the growing crystal surface, desolvated and arranged in conformity with the crystal structure. Both diffusion and convection are important in controlling the growth velocity. When the crystals are relatively smaller, convection may be neglected in view of the very low velocity of the growth fronts. At this stage, when convection is insignificant, crystal growth takes place essentially due to the steady diffusional concentration gradients. The fact that this state is established around the crystal at a much faster rate than the rate at which the

TABLE I

Temperature (° C)	ΔC_0 (g/g solution)	Rate constant $10^{-4}\,K_\mathrm{D}$ (cm² sec⁻¹)
700	0.029	0.0217
800	0.038	0.0522

solution in its close vicinity would be replenished, has been proved by Nielsen [23]. This also explains the initially faster growth rate. Such a situation exists up to an extent of 35% (corresponding to $\alpha_t \simeq 0.35$) and 56% (corresponding to $\alpha_t \simeq 0.56$) at 700° C and 800° C, respectively; the remaining growth may, nevertheless, be surface-reaction controlled.

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