

Turbidimetric study of fluorite nucleation in solution

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Abstract

Precipitation of fluorite (calcium fluoride) from solution at 30 and 37 °C has been studied by measurement of turbidity at different wavelengths, analyzing the data with the aid of the Mie theory of light scattering from small particles. In this way both number density and average particle size were obtained as functions of time. The values were confirmed by sedimentation analysis. In the later part of the process the results were strongly influenced by agglomeration and sedimentation, but the initial part of the curve of number density vs time was useful in determination of nucleation kinetics. The trend of nucleation frequency vs supersaturation agreed well with the classical theory of Becker, Döring, Volmer, Zel'dovich, and Frenkel, and surface energies equal to 102 mJ/m² at 30 °C and 89 mJ/m² at 37 °C were found. On the other hand, the absolute rate of nucleation was many orders of magnitude lower than that predicted by the theory, which is ascribed to an overestimate of the rate of growth of postcritical nuclei.

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1. Introduction

Light-scattering methods such as turbidimetry and nephelometry belong to the classical methodology of particle size determination ([1, Ch. 11] and [2,3]). It has been used in a number of investigations of crystallization kinetics, often as a replacement of visual determination of induction time [4,5], a rather primitive use, indeed, in view of its potentials. A somewhat more elaborate use of the gelation kinetics of ZnO/SiO₂ gels was presented in a paper appearing while the present manuscript was in preparation [6]. Compared to other methods of detecting the appearance and growth of a new phase, such as measurement of pH or conductance, it has the advantage that no probe has to be immersed in the supersaturated solution, as any foreign object could easily induce nucleation. The drawback is that it is useful only as long as the crystals remain suspended.

Most commercial instruments for particle size determination by light scattering make use of a monochromatic light source (i.e., a laser) and record the angular dependence of intensity of the scattered light. An alternative method, based on less

expensive equipment and used in the present investigation, is recording the turbidity spectrum at a fixed angle of 0°. Fluorite (CaF₂) has been chosen to test the method for the following reasons: (1) it has a simple crystal structure, belonging to the cubic system, which also means that its optical properties are isotropic; (2) it shows no polymorphism; and (3) its crystallization behavior is well known from previous studies by other methods.

Apparently the first extensive investigation on the precipitation kinetics of fluorite was carried out by Tovborg Jensen [7], using visual determination of induction time as well as recording solution conductance as a function of time. He did not arrive at a definite mechanism, but argued that the rate of crystallization is inversely related to single crystal hardness. Much later, part of his data on induction time were analyzed in terms of the mononuclear crystal growth mechanism by Nielsen [8], who found a surface energy at 296 K of 280–330 mJ/m², depending on the method of calculation. The connection of induction time with crystal growth rather than with nucleation was further confirmed in a more detailed analysis yielding edge free energies of 59 pJ/m at 291 K and 52 pJ/m at 296 K [9]. A similar analysis with analogous results was carried out for nanosized particles of ZnO/SiO₂ by Abel-Aal et al. [6].

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Further experimental studies by Nielsen and Toft [10] using conductance measurements and directed specifically toward crystal growth kinetics revealed the mechanisms of spiral growth at low supersaturation and surface nucleation at higher supersaturation. With the same method we found the polynuclear growth mechanism and edge free energies of 51 pJ/m at 298 K and 40 pJ/m at 310 K. These values are well in line with those from Tovborg Jensen's data for induction times. The crystals were mostly well-developed cubes with edge length about 1 μm at the latter temperature [11].

The aim of the present work is twofold: validation of turbidimetric measurements for crystallization studies and determination of nucleation kinetics of fluorite.

2. Theory

For spherical particles with diameters much smaller than the wavelength of light λ , the turbidity τ , assuming a cell of unit length, is given by the Rayleigh expression [2]

$$\tau = \frac{8\pi^3(n_1^2 - n_0^2)^2}{3\lambda^4 N}, \quad (1)$$

where n_1 and n_0 are the refractive indices of the particle and the surrounding medium, respectively, and N is the number density of particles. This expression shows no explicit dependence on particle size. For particles of larger diameter, but still $<\lambda$, the Rayleigh–Gans–Debye theory may be used. With particles of arbitrary size such as growing crystals only the Mie theory [3,12] is adequate. This theory provides no simple explicit expression such as (1). Instead, we have the extinction efficiency factor [3, p. 129]

$$Q_{\text{ext}} = \frac{\tau}{\pi N a^2}, \quad (2)$$

where a is the particle radius. Q_{ext} is typically expressed as a function of the relative refractive index $m = n_1/n_0$ and the variable

$$x = \frac{2\pi a n_0}{\lambda} \quad (3)$$

and may be found in different ways: using one of a large number of published tables [3, pp. 165–171], from a series expansion [3, p. 143ff], or, as in the present work, with the method of phase angles [3, pp. 135, 147–151]. We have

$$Q_{\text{ext}} = \frac{1}{x^2} \sum_{n=1}^{\infty} (2n-1)(2 - \cos 2\alpha_n - \cos 2\beta_n), \quad (4)$$

where the phase angles α_n and β_n are computed from

$$\begin{aligned} \tan \alpha_n &= -\tan \delta_n(x) \frac{\tan \alpha_n^*(mx) - 1 - m^2(\tan \alpha_n^*(x) - 1)}{\tan \alpha_n^*(mx) - 1 - m^2(\tan \beta_n^*(x) - 1)}, \\ \tan \beta_n &= -\tan \delta_n(x) \frac{\tan \alpha_n^*(mx) - \tan \alpha_n^*(x)}{\tan \alpha_n^*(mx) - \tan \beta_n^*(x)}, \end{aligned} \quad (5)$$

with

$$\tan \alpha_n^*(x) = -\frac{x j_n'(x)}{j_n(x)}, \quad \tan \beta_n^*(x) = -\frac{x n_n'(x)}{n_n(x)},$$

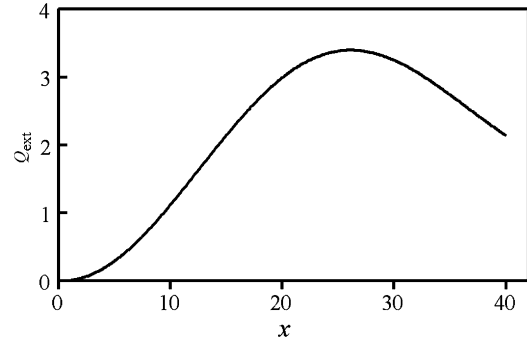


Fig. 1. Graphs of extinction efficiency factor Q_{ext} for fluorite in aqueous suspension.

$$\tan \delta_n(x) = -\frac{j_n(x)}{n_n(x)}. \quad (6)$$

j_n and n_n are spherical Bessel functions of the first and second kind, respectively. As more than 20 terms have to be included in the sum of Q_{ext} , an efficient algorithm for computation of Bessel functions is needed. Further details on the computation will be given in Appendix A.

Now the task is to find the value of a that makes the computed Q_{ext} proportional to the measured τ over the entire spectrum, which in the present investigation ranges from 300 to 800 nm. Fig. 1 shows Q_{ext} as a function of x for fluorite with $n_D = 1.434$ [13,14]. It turns out that a log–log plot of turbidity versus wavelength is approximately linear in the range $300 \leq \lambda \leq 800$ nm with slope > -4 , the lower limit agreeing with the Rayleigh expression (1). This means that the dependence of τ on λ is given approximately by a relation of the form

$$\tau = A\lambda^B, \quad (7)$$

where B , and possibly A as well, depends on a , and $B > -4$.

A plot of theoretical values of Q_{ext} versus λ yields a similar result, though, of course, with a different value of A , as shown in Fig. 2. Thus, we may determine a by trying different values in the computation of Q_{ext} for the different wavelengths, until the theoretical slope of $\ln Q_{\text{ext}}$ versus $\ln \lambda$ agrees with the experimental one of $\ln \tau$ versus $\ln \lambda$. We now have Q_{ext} for any wavelength in the range of measurement, and we finally obtain N from (2) by inserting a together with corresponding values of Q_{ext} and τ for one of the wavelengths.

A few points should be emphasized here. First, the determination of the slope of the log–log plot is subject to statistical uncertainty, because the linearity assumed is not exact. The uncertainty is highest in the range of the maximum on the curve in Fig. 1 corresponding to relatively large values of a . This is also evident from Fig. 2, which shows that the deviation of the theoretical plot from linearity increases with increasing a . An estimate shows, however, that even there the resulting standard deviation of a amounts to only about 1%, and in the lower range it is much smaller. Second, we have used in the calculations a wavelength-independent value of the relative refractive index, viz., $m = 1.075$. Using the actual dispersion spectra of water and fluorite [15,16], we find that this represents an average error of 0.2%. Finally, the above expressions apply to spherical

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