



# Kinetics of crystal growth of glycine manganese chloride in aqueous supersaturated solutions



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## ABSTRACT

In the present work, by using atomic force microscopy (AFM), the existence of periodic steps facilitates an aligned layer-over-layer (LOL) growth has been investigated for glycine manganese chloride (GMC) crystal. Nucleation and growth kinetics renders the information about the crystal growth process, which can be adopted to grow large size crystals. As for the crucial parameters in growing bulk crystal of GMC, the interfacial energy and growth activation energy have been calculated simultaneously from the induction time data without knowledge of the real growth rate of small nuclei. Additionally, various nucleation parameters involved in nucleation kinetics have been computed and described them as a function of temperature, degree of supersaturation. The results indicate that the growth activation energy for GMC is 13.34 kJ/mol, which suggests that the growth rate of small nuclei in the agitated induction time experiments is diffusion controlled.

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## 1. Introduction

In general, solution crystallization consists of two major kinetic events: nucleation and crystal growth. Nucleation plays a central role in the crystallization processes which largely determines the product quality such as crystal structure and size distribution of the crystals [1]. In recent years, nucleation study has been driven by a number of key developments: the availability of increasing computational power and improved simulation methods enabling the behavior of larger ensembles of molecules to be studied [2], the availability of off-the-shelf medium-throughput reactor devices for performing multiple repeats of identical experiments and, vitally, a range of easily accessible in situ microscopic and spectroscopic techniques [3]. However, classical nucleation theory remains the main framework describing a nucleation phenomenon [4]. Formation of crystal nuclei occurs in supersaturated (or supercooled) parent phase due to sufficiently large fluctuations. Small clusters have a tendency to diminish, and supercritical clusters (nuclei of a new phase) grow up to microscopic sizes. During this process, it is necessary to overcome a so-called nucleation energy barrier. The larger the value of the interfacial energy, the greater difficulty for the supercritical clusters needs to overcome. To our knowledge, induction time which has been well documented for measuring nucleation kinetics is the time between a supersaturated solution reaching to onset of nucleation [5–7]. It is worth noting that since the size of nuclei falls well below the detection limit of available instruments, turbidity detection methodologies are frequently used in practice to indicate the onset of nucleation [8–10]. Characterization of the induction time for a compound is considered to provide an important guideline for the design and operation of industrial

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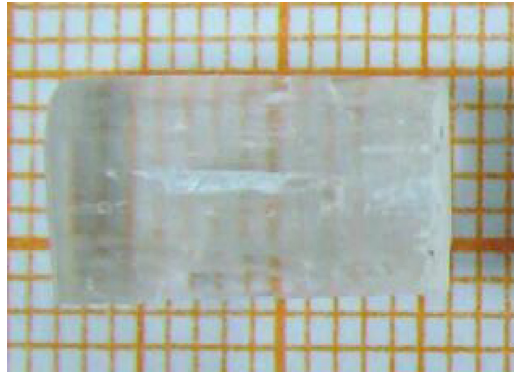


Fig. 1. Bulk crystal of GMC crystal.

crystallizers. The induction time influenced by several parameters including solvent species, temperature, concentration and so on.

A recently discovered promising nonlinear optical material, which can be used for the fabrication of opto-electronic devices such as routers and switches, is glycine manganese chloride (GMC) [11–13]. GMC crystallizes in a monoclinic structure,  $P2_1/c$  space group, with lattice parameters:  $a = 8.413(2) \text{ \AA}$ ,  $b = 5.613(2) \text{ \AA}$ ,  $c = 16.816(6) \text{ \AA}$ ,  $\alpha = \gamma = 90^\circ$ ,  $\beta = 90.165^\circ$ ,  $Z = 4$  and  $V = 794.1 \text{ \AA}^3$ . To date, few single-molecule investigations of glycine have been presented in literature, and no reports of GMC molecule primarily utilize atomic force microscopy (AFM) [14]. AFM is a powerful and widespread tool in biophysical research and is used both to image biological samples with nanometer resolution and to investigate single molecule nanomechanics by means of force spectroscopy method [15,16]. The present study utilizes AFM to obtain nanometer-resolution images of GMC molecules that have been deposited on atomically flat surfaces, with the aim of characterizing the GMC conformations that result from different levels of growth mechanism. In addition, as discussed before, detection of nucleation event and estimation of nucleation kinetics are important for successful design and operation of the crystallization process of GMC crystals. In the present work, both interfacial energy and growth activation energy have been acquired from induction time data without knowledge of the real growth rate of small nuclei.

## 2. Experimental and theory

The investigations were performed using a programmable computer-controlled microscopy system with a constant temperature bath, and a thermocouple placed into the bath was used to read the temperature of the solution. The turbidity probe (Crystal Eyes manufactured by HEL limited) was programmed to measure the turbidity of the solution. Accordingly, observations of the changes in nucleation versus time can be recorded. Supersaturated solutions were prepared by mixing dissolving equimolar glycine and manganese chloride. The solution was filtered through a series of  $0.45 \mu\text{m}$  membrane filters and the crystals were obtained by temperature lowering solution growth method. After a span of 50 days, transparent samples can be harvested (Fig. 1). In the measurements of induction period ( $t_{\text{ind}}$ ), initially, the solution was heated 5 K above the saturation temperature for 5 h. The supersaturation ratio which explored here is defined as  $S = C/C_{\text{eq}}$ , ranges between 2.5–1.3, where  $C$  and  $C_{\text{eq}}$  refers to actual and equilibrium concentration, respectively. Every experiment was repeated at least three times to ensure reproducibility, and the average value for the  $t_{\text{ind}}$  was used in the analysis of the final results.

According to classical nucleation theory, the primary homogeneous nucleation rate for spherical particles formation is given by [17]

$$J = A_J \exp\left(-\frac{E_G}{kT}\right) = A_J \exp\left(-\frac{16\pi\gamma^3\Omega^2}{3k_B^3T^3\ln^2 S}\right) = A_J \exp\left(-\frac{B}{\ln^2 S}\right) \quad (1)$$

where  $A_J$  is pre-exponential factor;  $E_G$ , an activation free energy for nucleation;  $\gamma$ , interfacial energy between crystal and aqueous solution;  $\Omega$ , molecular volume of the crystal ( $1.99 \times 10^{-28} \text{ m}^3$  for GMC);  $k_B$ , Boltzmann constant ( $1.38 \times 10^{-23} \text{ J/K}$ );  $T$ , absolute temperature;  $B$ , a constant  $= 16\pi\gamma^3\Omega^2/3k_B^3T^3$ . When growth supersaturation is low in the present induction time experiments, the empirical power-law growth rate verified by Mohan and Myerson is generally of the form [18]:

$$G \doteq k_G (\ln S)^2 = A_G \exp\left(\frac{-E_G}{RT}\right) (\ln S)^2 \quad (2)$$

where  $A_G$  is a kinetic growth factor. In terms of the general expression reported by Shiau et al., minimum detectable projected area density of accumulated crystals in the detector direction at the induction time  $t_{\text{ind}}$  as [19]:

$$f_A = \frac{Jk_A G^2 t_{\text{ind}}^3}{12} \quad (3)$$

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