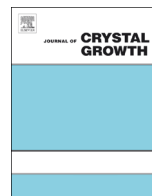




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Nucleation kinetics and growth aspects of negative solubility lithium sulphate monohydrate single crystal



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ABSTRACT

Nucleation and growth kinetics give valuable information about the crystal growth process, which can be employed in the growth of large size crystals. Accordingly, this paper discusses nucleation theory as applied to crystallizing negative solubility lithium sulphate monohydrate (LSMH) crystal. Solubility, metastable zone and induction period values were determined experimentally in order to optimize the growth parameters. The nucleation parameters such as interfacial energy, volume free energy, critical free energy and critical radius have been evaluated. The results have been discussed in detail. The good quality single crystal of LSMH was grown by the low temperature solution growth technique. The growth and dislocation behaviors were detected under the etching studies. It is shown that the classical approach explains the available nucleation data under most conditions used for growing LSMH crystals.

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1. Introduction

Lithium sulphate monohydrate ($\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$) has good piezoelectric and nonlinear optical properties [1–5]. It has been studied to great extent over several decades as it is a high temperature superionic conductor [6,7]. Nonlinear optical materials have gained importance due to their pertinent properties such as high laser damage threshold, wide transparency range and high nonlinear coefficient [8–10]. Due to specific properties of such kinds of the crystal one can expect that it would be a potential candidate for NLO applications. It is seen from the literature that lithium on its combination with materials like glycine, selenate, potassium and borate proves to be highly NLO active. Also, many new crystals in the lithium sulphate family are excellent NLO materials [10–15]. The detailed structure analysis of the title compound is already reported [16–19]. The crystal structure is built up from corner sharing $(\text{SO}_4)^{2-}$ anions, Li^{2+} cations that are connected by oxygen atoms to a three dimensional network. In addition the transition of lithium sulphate from a very low symmetry monoclinic structure to a disordered plastic phase is associated with a progressive dynamical decoupling between the SO_4^- and Li^+ ions, as well as with a progressive decrease in the spatial correlation between the

polyatomic anions which has been compensated by taking one of its water molecules.

However, the grown LSMH crystals have some defects and the transparency was poor [5,15]. In order to grow crystals with optical qualities for nonlinear applications, a systematic investigation of optimized growth conditions has been carried out in our laboratory. As the driving force that leads to nucleation and crystal growth, solution supersaturation and other growth conditions should be determined and optimized. We are interested to study the nucleation thermodynamical parameters like interfacial energy and Gibb's free energy change from the experimentally determined values of induction period, supersaturation and metastable zone width (MZW) based on the homogeneous nucleation theory. As no such report is available in the literature, the present study would be very useful to optimize the growth parameters to get large size single crystals with good optical quality with controlled and undisturbed growth throughout the growth period.

2. Experimental, results and discussion

2.1. Solubility and metastable zone width

The size and growth rate of a crystal depends on the solubility and temperature of the solution. According to thermodynamics, when the chemical potential of the pure solute in the saturated solution is equal to the chemical potential of the same solid is called

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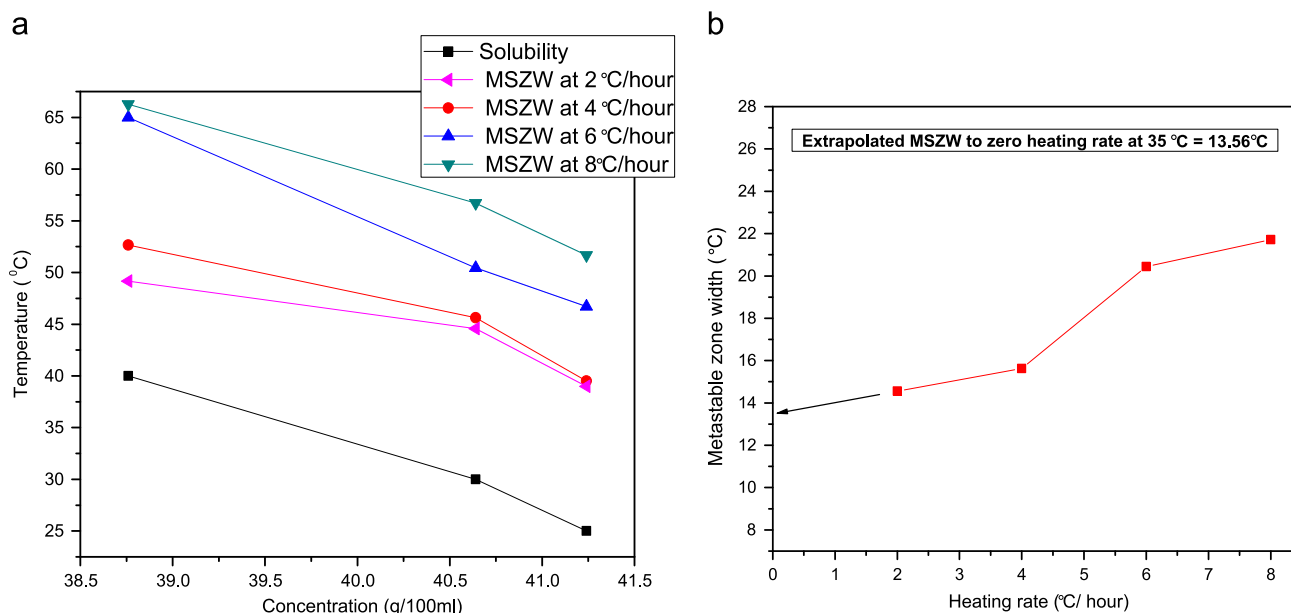


Fig. 1. (a) Solubility and MSW of LSMH (b) MSW of LSMH for different heating rates at 35 °C.

solubility, which depends on temperature and pressure. The solubility of LSMH was estimated from 30 to 50 °C in steps of 5 °C using water as a solvent. A volume of 100 ml of water was taken in a beaker and known quantity of the material was added till it attains saturation for different temperatures. The solubility curve of LSMH is shown in Fig. 1(a). It shows that concentration of solute in the aqueous solution decreases for increasing temperature because of the negative solubility behavior of LSMH. The negative solubility effect occurs when the solute dissolves in its near-saturated solution with an evolution of heat (exothermic heat of solution). The solubility of LSMH was found to be 32.81 g/100 ml at 40 °C.

Metastable zone width (MZW) is important for many experiments in crystal growth processes that carefully control the number of nuclei and crystallites under conditions where the supersaturation varies in time. The stability of the growth solution with wide metastable zone width is important for the growth of bulk crystals. For nucleation in micro droplet arrays, the MZW is the average supersaturation at which the first nucleus forms when the supersaturation is steadily increased by solvent evaporation. The difference between the saturated temperature and the nucleation temperature is taken to be the metastable zone width of the system. The value of the metastable zone width depends not only on the temperature but also on the type of the crystal and its physicochemical properties. MZW of LSMH solution was measured by the conventional polythermal method [20–22]. In polythermal method, the equilibrium-saturated solution is cooled from the overheated temperature till the temperature at which the first visible crystal nucleus (primary nucleation) is observed. But this is directly opposite to the negative solubility materials like LSMH. Saturated solution of LSMH was prepared for the nucleation experiments. The nucleation experiments were carried out in a constant temperature bath with an accuracy of ± 0.01 °C, provided with cryostat for cooling below room temperature. A constant volume of purified LSMH of 50 ml was used in all the experiments. The saturated solution was cooled to 5 °C below the saturated temperature for homogenization and left at the super-cooled temperature for 1 h before heating. The solution was continuously stirred using a motorized stirrer to ensure homogeneous concentration and temperature in the entire volume of the solution. The temperature of the bath was increased at a rate of 4 °C/h with continuous stirring after the homogenization. Since

the time taken for the formation of first visible nucleus after the attainment of critical nucleus is very small, the observation of first nucleus may be taken as the critical nucleus [23,24]. Several trials were performed to find the optimization. MZW was measured again to different heating rates (2 °C/h, 6 °C/h and 8 °C/h). Fig. 1(a) shows the MZW curve for different heating rates. The same has been extrapolated to zero heating rate, which is 13.56 °C of LSMH at 35 °C (Fig. 1(b)). It can be seen that the larger heating rate is the reason for larger the MZW. The LSMH solution has broader MZW (ranging in the extent 10–21.70 °C) compared to several positive solubility materials [24–27]. The larger metastable zone width at all temperatures greatly avoids the secondary nucleation formed during crystal growth. So, bulk crystals can be effectively grown from the slow evaporation or slow heating technique.

2.2. Induction period

The study of the induction period against supersaturation gives an idea of the optimized induction period in order to have controlled nucleation rate to grow good quality single crystals. In order to find the induction period for LSMH at different supersaturation, the conventional isothermal method was used [28,29]. The induction period t_i is the time period during which the supersaturated solutions could be stable without spontaneous crystallization. The prepared supersaturated solutions were cooled 10 °C below the saturation temperature for homogenization and then were taken to the desired temperature. When the desired temperature and concentration were reached, the solution was maintained at that temperature and the time taken for the formation of the first crystal (primary nucleation) was measured. The procedure was repeated for various supersaturation values at a particular temperature 40 °C and the corresponding time was investigated. Repetitious experiments were carried out to calibrate the observed results. Fig. 2 represents the induction period as a function of the solution supersaturation. It was observed that the induction period decreases with increase in supersaturation.

2.3. Crystal growth

To grow single crystals of LSMH slow evaporation solution growth technique (SEST) was employed. High purity LSMH [SRL

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