Preparation and characterization of some single, mixed and doped crystals and instrumentation aspects

R KRISHNASWAMY
Reactor Research Centre, Kalpakkam 603 102, India

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Abstract. The preparation and characterization (salient ones) of KAl(SO₄)₂·12H₂O, KCr(SO₄)₂·12H₂O, mixed crystals of both with 10 to 90% of each component, mixed crystals of CsCl with CuCl₂, doped crystals of KBr with K₄FeCN₆, mixed crystals (NH₄)₂SO₄ with CuSO₄ or NiSO₄, NaCl with growth improver Pb²⁺, Mn²⁺, metallic crystals of Zn, Bi, ionic crystals of alkali halides with Pb²⁺, or Cd²⁺, etc. are presented. Instrumentation aspects of a rotary crystallizer, a homogeniser, an ingot release mechanism and a zone refiner are shown.

Keywords. Common ion effect; crystal defects; crystal growth; growth improvers; ingot release mechanism; melt method; zone refiner.

1. Introduction

The advent of growth of crystals, thin films, layered materials, ferroelectrics and metallic glass with their wide range of useful properties, has given an impetus to the preparation and characterization. This aspect is important for efficient working of the device and for obtaining unambiguous experimental results. Problems such as oxidation, vapour pressure, dissociation, non-stoichiometry, peritectic formation widely different liquid-solid densities, etc also need to be overcome. After the advent of the transistor in 1948, these aspects in the crystal growth industry have gained importance, as the materials have to be characterized and the impurities removed. The growth of exotic compounds, e.g. yttrium, aluminium garnet (Mac Innes 1972) for use in laser work, GaAs in laser, etc. provided further impetus. The characterization is usually done by (i) physical means or (ii) chemical means including spectrochemical methods. In physical methods one uses the Laue pattern, etch pattern, dislocation density, microscopic study, resistivity and resistivity ratio (R 300/R₄.2°K), conductivity, Hall effect, x-ray powder pattern, etc. to characterize the sample. In chemical methods, one uses qualitative, quantitative and spectroscopic methods to characterize the sample, to study the nature and extent of impurities. Both the methods are complementary as the second one helps to confirm the presence, the extent and estimation of the error factor in the results. This aspect of preparation and characterization has been given only a passing mention in many of the publications, relating to the Raman effect, Brillouin scattering, electroluminescence, etc.
The preparation and characterization of mixed crystals of KA\(_2\) (SO\(_4\))\(_2\), 12H\(_2\)O, and KCr (SO\(_4\))\(_2\), 12H\(_2\)O (mixed alums), CsCuCl\(_3\) (mixed crystal of CsCl and CuCl\(_2\)), mixed crystals of KBr with K\(_3\) FeCN\(_6\), doped crystals of alkali halides with Pb\(^{2+}\), Cd\(^{2+}\) and rectification of some of the problems are presented in this paper. The standardization of the preparation is also dealt with. Difficulties encountered in the characterization and some of the instruments developed for efficiency are also presented.

2. Rotary crystallizer

The rotary crystallizer (Krishnaswamy 1978) is used for crystal growth, by the supersaturation method, of materials having solubility-temperature gradient \(\geq 0.5\) g/°C for 100g of solvent and which have reversible and positive solubility gradient. It is also used for materials which decompose on heating, e.g., ammonium salts and other cases and where strain-free crystals grown in their natural facets are needed. The unit is shown in figures 1a and 1b. It has a 2-speed automated constant time (84, 204 sec.) stirrer reversal for prevention of inclusions, edge growth and other crystal defects. It uses a new electronic multivibrator circuit and relay, which is advantageous than the conventional cam method. The crystallizer has a variable temperature gradient provision (up to 24 hr/°C), to suit the growth habit, solubility-temperature gradient and to keep the mass transfer to the growing crystal under control in a unilayer fashion.

Figure 1a shows the rotary crystallizer with all its details and figure 1b shows the schematic of temperature gradient control. The gradient expression is shown in equation (1)

\[
\text{temperature gradient with } \frac{1}{\text{time (h/°C)}} = \frac{1}{1 \text{ rev}} \times \frac{60 \text{ min}}{\text{rev}} \times \frac{D_1}{D_2} \times \frac{D_3}{D_4} \times \frac{D_5}{D_6} \times \frac{°\text{C}}{2 \text{ rev}}
\]

The final pulley \(D_6\) is coupled to the on/off controller of the thermostat, through a 20-cm pulley, fixed to the top of the controller shaft and using a 2-mm thick, 150 mm diameter O-ring as a belt. Change of \(D_6\) effects the desired variation. Crystals grown in this crystallizer using supersaturation method are KA\(_2\) (SO\(_4\))\(_2\), 12H\(_2\)O, KCr (SO\(_4\))\(_2\), 12H\(_2\)O (potash and chrome alum), mixed crystals of both with 10-90% of one component, mixed crystals of CsCl with CuCl\(_2\) as CsCuCl\(_3\) doped crystals of KBr, with K\(_3\)FeCN\(_6\), mixed crystals of (NH\(_4\))\(_2\)SO\(_4\) with CuSO\(_4\) or NiSO\(_4\), NaCl with growth improver Pb\(^{2+}\), Mn\(^{2+}\) and NaCl, KBr, etc by evaporation method. The maximum size obtained was 45 mm across. The complete unit is shown in figure 2 with all subunits marked for identification.

Growth of single and mixed crystals

Single crystals, for example octadecahedral Ni (SO\(_4\)) \(_7\) H\(_2\)O was grown from good quality seeds of 5 x 5 x 2 mm size using the crystallizer as shown in figure 1a and 1b. The crystal was obtained after 15 days run at a gradient of 1°C/18 hr from 45°C. The temperature control was ± 0.05°C and as a continuous