

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

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Abstract. The preparation and characterization (salient ones) of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, mixed crystals of both with 10 to 90% of each component, mixed crystals of CsCl with CuCl_2 , doped crystals of KBr with K_3FeCN_6 , mixed crystals $(\text{NH}_4)_2\text{SO}_4$ with CuSO_4 or NiSO_4 , NaCl with growth improver Pb^{+2} , Mn^{+2} , metallic crystals of Zn , Bi , ionic crystals of alkali halides with Pb^{+2} , or Cd^{+2} , 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 ($R_{300}/R_{4.2}^\circ\text{K}$), 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 $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, and $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (mixed alums) CsCuCl_3 (mixed crystal of CsCl and CuCl_2), mixed crystals of KBr with K_3FeCN_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 $\cong 0.5 \text{ g/}^\circ\text{C}$ 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 $24 \text{ hr/}^\circ\text{C}$), 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)

$$\text{temperature gradient with time (h/}^\circ\text{C)} = \frac{1}{\left\{ \frac{1 \text{ rev}}{\text{min}} \times \frac{60 \text{ min}}{\text{hr}} \times \frac{D_1}{D_2} \times \frac{D_3}{D_4} \times \frac{D_5}{D_6} \times \frac{^\circ\text{C}}{2 \text{ rev}} \right\}} \quad (1)$$

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 $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (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_3FeCN_6 , mixed crystals of $(\text{NH}_4)_2\text{SO}_4$ 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 $\text{Ni}(\text{SO}_4) \cdot 7\text{H}_2\text{O}$ was grown from good quality seeds of $5 \times 5 \times 2 \text{ mm}$ size using the crystallizer as shown in figure 1a and 1b. The crystal was obtained after 15 days run at a gradient of $1^\circ\text{C}/18 \text{ hr}$ from 45°C . The temperature control was $\pm 0.05^\circ\text{C}$ and as a continuous

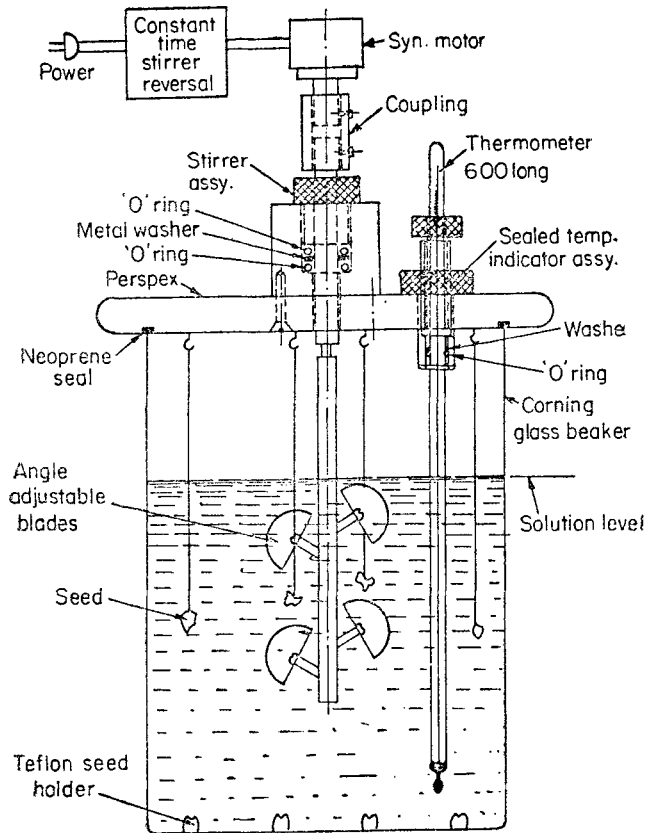


Figure 1 a. Rotary crystallizer.

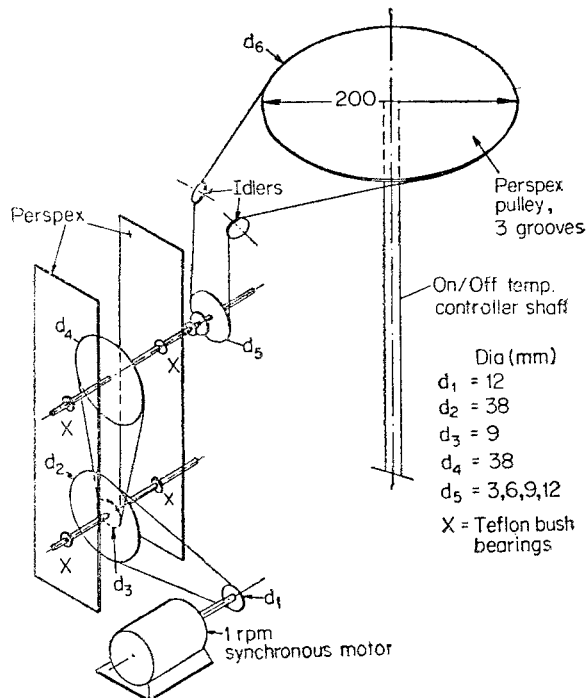


Figure 1 b. Schematic of temperature gradient control.

Table 1. Common ion effect on solubility

Component, order (weight)	Solubility $T = 26^{\circ}\text{C}$ (g/100 cc)				$T = 45^{\circ}\text{C}$ (g/100 cc)			
Chrome alum (I)	-	4.0	10.0	-	4.0	10.0	-	
Potash alum (II)	13.24	11.09	8.57	24.7	23.51	19.52		
Potash alum (I)	-	4.0	10.0	-	4.0	10.0	20	
Chrome alum (II)	23.8	16.8	6.75	53.8	43.8	32.71	13.47	

Note: Values determined experimentally.

lowering method was used (figure 1b) the temperature profile was smooth which helped in crystal perfection. The other single crystals of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, KDP, ADP were grown by a similar method.

The mixed crystal means single crystal having crystal symmetry and shape (either octahedral, hexagonal or octadecahedral) depending on the nature of the crystal with one constituent growing in the other in substitutional or interstitial spaces. Detailed theoretical treatment on certain aspects is given elsewhere (Petrov 1969, Khamskii 1964). In the mixed crystal for example $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ the common ion effect is one factor. It is known that in the presence of a common ion, the solubility of the second component decreases, and if the first component is in saturation, there is precipitation of the excess of the first component. For example, the sparingly soluble AgCl has a solubility product (K) of 1.2×10^{-10} units. The solubility of each ion is 1.1×10^{-5} M which decreases to 10^{-9} M on addition of 0.1 M NaCl due to the common ion effect of Cl^- , as shown in equation (2)

$$X(X + 0.1) = 1.2 \times 10^{-10} = K, X = 1.2 \times 10^{-9} \text{ M} \quad (2)$$

Similarly both potash alum and chrome alum have K^+ , SO_4^{-2} as the common ion. The common ion effect on the solubility of the second component is shown in table 1 for mixed alums.

It shows clearly the effect of common ions, K^+ , SO_4^{-2} in reduction of solubility of component (II). The values are for components added in order and not for random precipitation, or mass transfer which can happen in the growth of a mixed crystal. The effect can be approached in the form as shown for AgCl in equation (2)

$$X(X + 0.05)^3 = K \quad (3)$$

using simulated values for X (upto saturation limit) and 0.05 M as the addition of second component. This is a 4th order equation with 4 roots. The best fit has to be obtained using least square fit computer programs and the 3rd and 4th order roots can be obtained only by simulation. The validity of this approach is to be ascertained, and even if it is suitable, it may not fully solve the stoichiometry

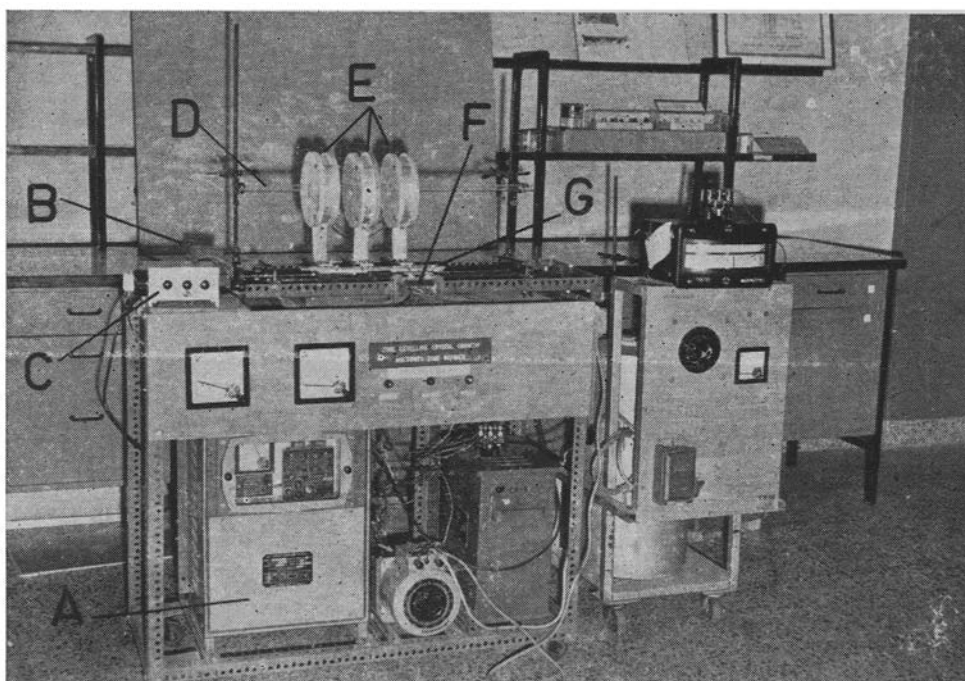


Figure 2. Rotary crystallizer-complete unit (A) Constant time stirrer reversal (controls) (B) Height adjustable jack (C) Screw for height adjustment (D) Variable temperature gradient control (E) Temperature controlled bath (F) Rotary crystallizer (G) Viewing window

of the mixed crystal, as it is a random precipitated sample. As a first approximation, one takes X and Y g of potash alum (I) and chrome alum (II) as per ratios shown in table 1. The final stoichiometry is $(X-13.24) : (Y-25.8)$ in percentages as a first approximation taking each solubility into account.

For example, starting with 25 g, 34 g of potash alum and chrome alum, the final stoichiometry was estimated as 65% : 35% (but the results were 72% : 28% of potash alum and chrome alum respectively.) (The potash alum value was higher in the mixed crystal and in the settlement at the bottom showing that the common ion effect in potash alum was predominant.) Further precipitation of potash alum is more as chrome alum solubility limit is not reached (see table 1). The error for this approximation was $\pm 12\%$ and no doubt with more work in this field, on the lines shown, the error factor may improve and the programmed mode of mixed crystal growth will be a reality.

4. Characterization of mixed crystals

4.1 *Mixed crystals of alums - discussion*

Mixed crystal comprises of potash alum and chrome alum. A light or dark tint of violet in crystal indicates chrome alum but not potash alum. K occurs in both alums varying in percentage from 7.97% to 7.8% (by weight) for pure potash alum to pure chrome alum. As the difference is very small, estimation of K as $K_2Na(CO(NO_2)_6)H_2O$ (dipotassium sodium cobaltinitrite) though this method is applicable in the presence of sulphate. This method will lead to large errors as Cr occurs in chrome alum only. In pure chrome alum to mixed alum (70%) though the variation is comparatively large (10.4 to 7.4% Cr) the range is small and will lead to errors. For example, in 2 trials it showed 9.9% and 9.4% Cr. It may be pure chrome alum (10.4% with 10% error) or mixed crystal as violet colour is not confirmatory and specific. Al occurs in potash alum only. Al estimation as oxinate ($Al(C_9H_6ON)_3$) gravimetrically allows the weight to vary from 0-459 gm for pure chrome to pure potash alum respectively. The range is very large and the chances of error are negligible. Initial to complete precipitation occurs at 2.9-4.7 pH. The interference is from Ca, Co, Ni, Zn, W, Fe^{+3} at these pH values (Vogel 1960). Starting materials do not exceed a total of 0.1% in the above. The maximum possible error is 0.4% and is within tolerance. The stoichiometry estimation is shown in equation (4)

$$K = A \times 0.0588 \times \text{mol wt. of pot. alum (474.4)}, \quad (4)$$

K = wt. of potash alum, A = wt. of oxinate. Chrome alum is found by the difference. The Al estimation was done colorimetrically as aluminium haematoxylin at 610 and 730 nm. The difference in optical density between the two is due to Al, as iron interferes at 610 nm and shows absorption separately at 730 nm. The oxinate values were within tolerance ($\pm 5\%$) confirming the suitability of oxinate method. The x-ray powder pattern was unsuccessful due to overlapping of lines and nonavailability of sophisticated diffractometer with good resolution.

Table 2. CsCuCl_3 characterization data

d (\AA)	2.78	3.61	4.35	6.25	2.175	3.03	2.726
I/I	100	90	75	16	25	25	30

4.2 CsCuCl_3 mixed crystals and growth improvers

Mixed crystals of CsCuCl_3 were formed from CsCl and excess of CuCl_2 (to prevent the formation of CsCuCl_4). The mixed crystal is brown-red in colour and has a distorted hexagonal bipyramid shape. The powder data shown in table 2, were used in characterization (Powder Diffraction File 1972).

The absence of free CsCl and CuCl_2 was characterized by the absence of corresponding lines (Powder File 1974 a,b).

Growth improvers in the form of foreign ions have been found helpful in many cases (Gilman 1963) in supersaturation method. For sodium chloride, Mn^{+2} and Pb^{+2} act as growth aids (Brice 1973) in concentrations ranging from 2–5 mM. The chlorides were used for common ion effect. Cubic, transparent, $8 \times 8 \times 3$ mm size crystals were obtained using growth aid whereas the conventional method yielded translucent and imperfectly shaped crystals in a smaller size. The mechanism suggested was the growth aid which stabilizes the metastable phase improving the solubility gradient in the nucleation stage. The growth aid

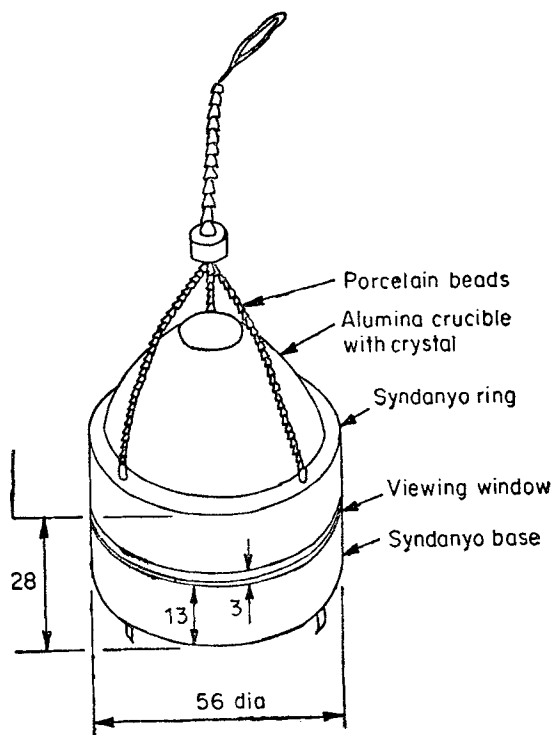


Figure 3. Ingot release mechanism.

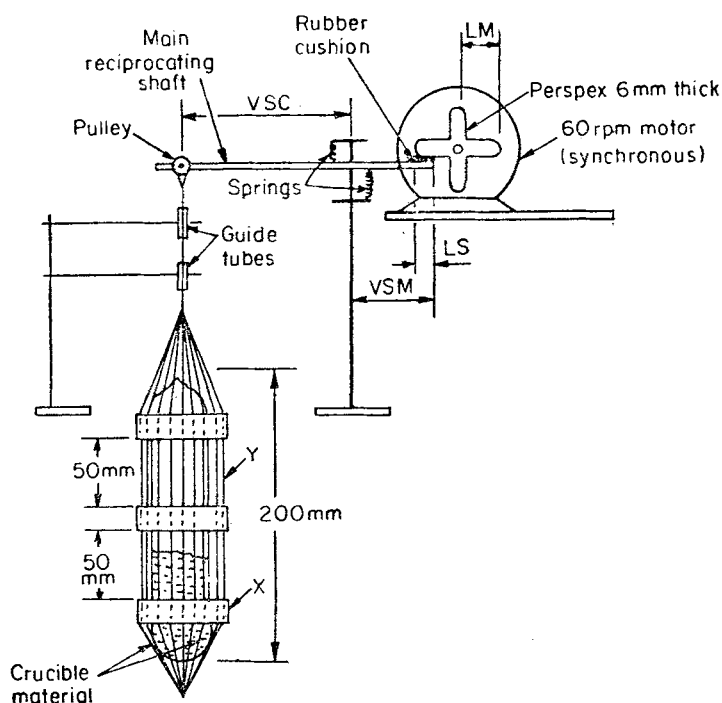


Figure 4. A new homogenizer; VSM—Vibrating shaft (Motor) 3.7 cm; VSC—Vibrating shaft (Crucible) 16.2 cm; LS— $1/2$ LM=2.5 cm I—Kanthal wire 22 swg; X—Heat insulating Syndanyo cushion ring, 2.5 cm dia.

inclusion in the crystal was nil, as tested by chemical means. These aids were useful especially where criteria as shown in § 2 were not met fully.

5. Preparation of doped crystal by melt method and innovations

The growth of crystals by melt method using Bridgman-Stockbarger method is known for a long time now (Bridgman 1925, Brice 1973). NaCl, Pb⁺² or Cd⁺² (as chlorides) doped NaCl, KBr, Zn, Bi were grown in open or sealed crucibles. For NaCl, the wetting and sticking to the walls of quartz or alumina crucibles was a problem. The wetting could not be eliminated even after repeated drying of the starting sample in vacuum at 400°C. To overcome this difficulty an ingot release mechanism as shown in figure 3 was built. The crucible with ingot is loaded into the cage and when the furnace temperature is 20°C above melting point, the ingot release mechanism is introduced for 5–10 min, where the crystal gets released as felt by the difference in pull and sometimes by visual inspection. Immediately the ingot is transferred in full to an annealing furnace kept ready, to prevent further melting of the ingot. It is now done by visual checking and further improvement with alarm indication of the release is being attempted. The strain to the crystal is kept low by allowing it to fall as low a distance as

possible (3-5 mm) and further fall will be cushioned by the syndanyo, which is heat-resistant up to high temperature.

In the crystal growth of Cd^{+2} , Pb^{+2} doped crystal growth of NaCl by the melt method, the dopant level was 150 ppm (molar). Normally, the dopant concentration ions should be uniform along the ingot mainly due to diffusion, and the tolerance allowed. In the case of Pb^{+2} in NaCl repeated trials indicate that the levels were not uniform. They were 88, 210, 230, 107, 487 ppm necessitating the development of a homogenizer as shown in figure 4. The result of a trial of In-Cd (95.5 at.% In) showed improvement in standard deviation of the final stoichiometry taken from 10 electron probe readings along the length of the ingot. It improved from 0.69% to 0.44%, 0.34% and 0.29% for 0, 2, 10 and 24 hr homogenization. In-Cd alloys need homogenization, as In-Sb compounds do. A visual check on the efficiency of the homogenizer was obtained by the total pink colour of 2-3 cc of NaOH and 2 drops of phenolphthalein in just 1 min and without homogenization, the thorough mixing took 30 min, at standstill, by diffusion alone.

A metallurgical sample of aluminium with 4 at.% copper showed satisfactory ductility and critical deformation ability to produce a single crystal only after homogenization. The jerk was kept at 2 cm (see figure 4) and the efficiency is maximum and time required is less if the melt height equals jerk length (Krishnaswamy 1980).

The Pb^{+2} doped NaCl showed dopant levels at 169, 131, 148, 138, 127 ppm (molar), for 2 trials after 2 hr homogenization at melting point as ascertained by atomic absorption spectra of Pb^{+2} . It shows that the uniformity (from 179.7% to 18.7%)* is better than without homogenization and with increase in homogenization period the results are bound to be better.

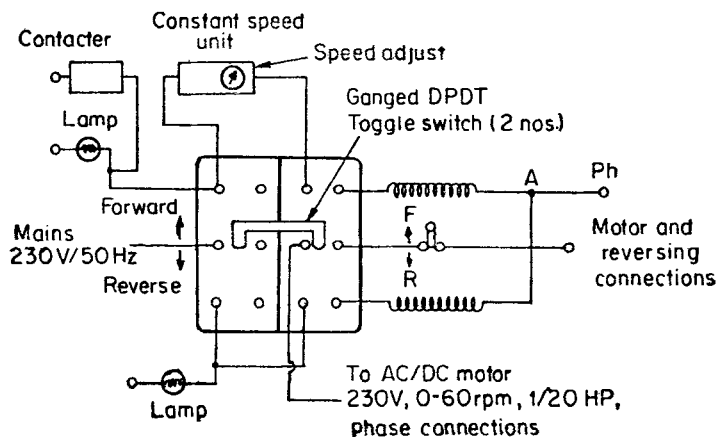


Figure 6. Schematic of zone-refiner automation.

*The details of the built assembly can be sent on request.

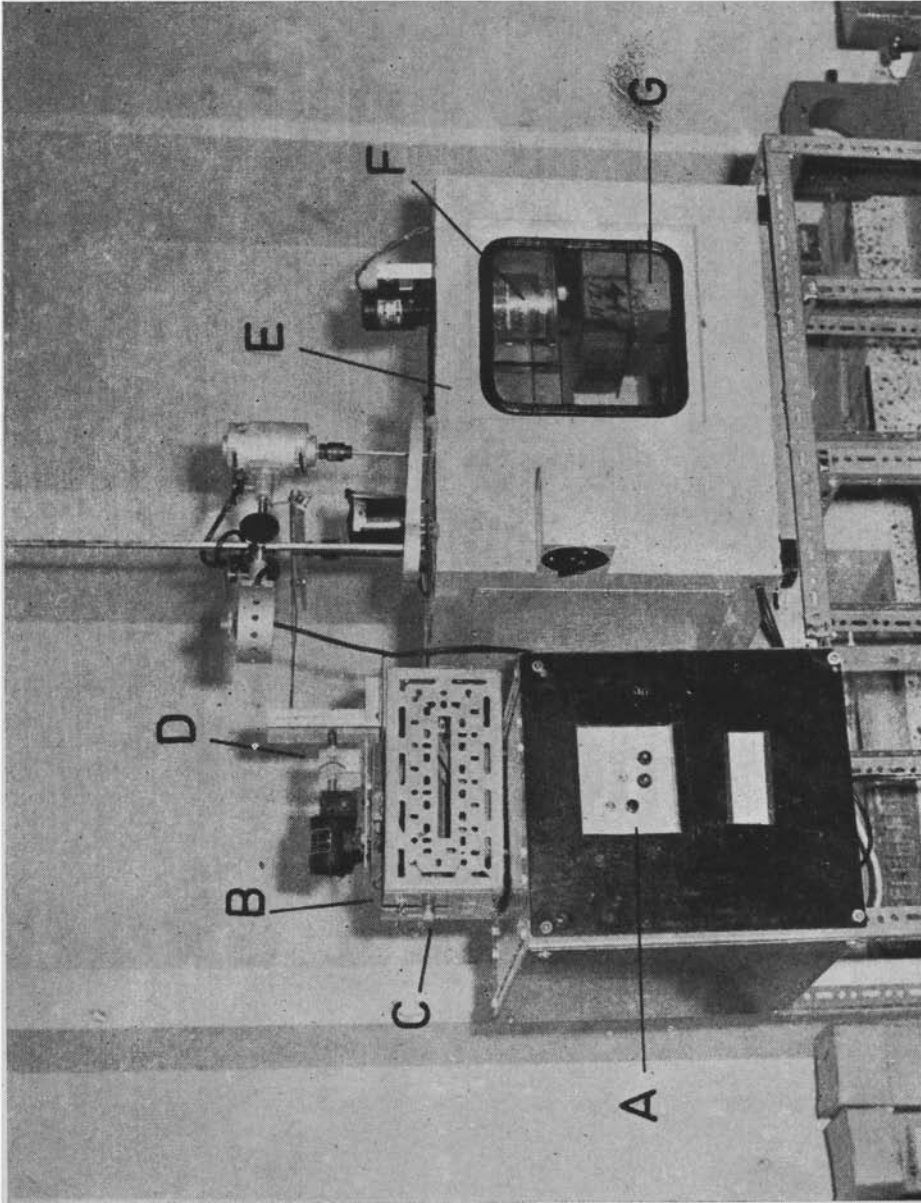


Figure 5. A multipass automated zone refiner (A) Constant voltage-power supply (B) Motor 1-60 RPM, reduction gear (C) constant speed unit (D) Quartz tube with boat (E) Heaters (F) Automatic reversal- \pm 4pdt switches (G) Length compensator $\times 2$

In the preparation and characterization field, zone refiner has unusual advantages as very high purity materials can be made (Pfann 1966). As pure materials are needed in the preparation of crystals, a variable speed zone refiner was built as shown in figure 5. It has the advantages of a constant torque circuit coming into operation only in the slow forward speed (variation from 2 cm/h to 8 cm/h) and an automatic reversal at 10 cm/min by a twin $d\text{pd}T$ switch mechanism using a single motor only. The schematic is shown in figure 6. The constant torque circuit uses SCR control by the back EMF of the motor, which in turn depends on the difference between the set speed and the actual speed. The firing time is advanced when the speed is reduced and vice versa helping constant torque operation. The constant torque electronic assembly is at present satisfactory at 2 cm/hr to 8 cm/hr forward speed. Further speed lowering to 0.1 cm/hr is under progress using a Cole-Parmer fractional horsepower motor. The constant torque assembly is bypassed in the reverse speed (figure 6) as it is superfluous at 60 RPM. Zinc was refined and characterized by $R_{300}/R_{4.2}^{\circ}\text{K}$ rat

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