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Synthesis of ZnO single crystals by the flux method

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Zinc oxide (ZnO) single crystals have been grown at temperatures ranging from 450–900 °C and for 1–12 h, using hydrous KOH and NaOH melts as fluxes. For a KOH flux, brown ZnO single crystals with diameter 0.5 mm × 7.5 mm were grown under conditions of 500 °C for 20 h and white crystals of diameter 0.5 mm × 7 mm were grown at 800 °C for 20 h, using a small crucible (average 50 ml). When a large crucible (average 400 ml) was used, ZnO single crystals with diameter 0.5 mm × 8 mm were formed at 900 °C for 30 h. When using a KOH + NaOH (1 : 1) flux, light-brown and long crystals with diameter 1.0 mm × 18 mm could be grown. The grown ZnO single crystals were bounded with only both p- and m-faces. It seems that crystal qualities were good under conditions of 900 °C for 30 h. The following mechanisms of dissociation and formation of ZnO single crystal from KOH (or NaOH) + ZnO melt seemed to occur

$$\mathrm{KOH(or\ NaOH)} \rightarrow \mathrm{K^+\ (or\ Na^+)} + \mathrm{OH^-}$$

$$\mathrm{ZnO} + 2\,\mathrm{OH^-} \rightarrow \mathrm{ZnO_2^{2-}} + \mathrm{H_2O},$$

$$\mathrm{ZnO_2^{2-}} \rightarrow \mathrm{ZnO} + \mathrm{O^{2-}}.$$

1. Introduction

Zinc oxide (ZnO) is a hexagonal (hemimorphic class) crystal of the wurtzite-type structure and its space group belongs to F43*m*. This class has the same six vertical planes of symmetry meeting at angles of 30° in the vertical crystallographic axis which is an axis of hexagonal symmetry. There is no centre of symmetry. The atoms of zinc and oxygen are tetrahedrally co-ordinated by four of the other kind. The dimensions of the bimolecular hexagonal unit are $a_0 = 0.3250$ nm, $c_0 = 0.5207$ nm.

The oxide is known for its earliest uses as a pigment in paints and in medicine and rubber, glass, porcelain enamels and pharmaceuticals. More recently, zinc oxide has found new applications in such products as phosphors, ferrite, varistors of surface elastic wave filters, ZnO-based non-linear resisters, solid state hydrogen and ammonia gas sensors, semiconductors, photosensitive materials used as electrographic copying paper, luminescence, ferromagnetism, etc.

Zinc oxide single crystals have been reported to be grown by employing vapour-phase and liquid-phase techniques. In the former, several researchers have studied the hydrolysis of a zinc compound [1, 2], chemical vapour transport [3], and sublimation of a zinc compound [4, 5], or zinc [6, 7]. In the latter, the hydrothermal technique [8–11], growth from stoichiometric melt [7], and high-temperature solution growth [13–17], were attempted.

Thin needles of ZnO have been grown at 400 °C by Kashyap [18], employing hydrous KOH as a solvent.

The purpose of the present work was to investigate the detailed growth conditions of large ZnO single crystals at temperatures ranging from 450–800 °C and for 1–92 h, from the evaporation of the flux.

2. Experimental procedure

Hydrous KOH and NaOH were used as the flux, with ZnO as a nutrient. All reagents were of special grade. In order to determine the concentration of H_2O in the hydrous KOH and NaOH, these aqueous solutions with a known volume were titrated using a standardized 0.1 M HCl solution using methyl orange as an indicator.

Two iron crucibles were used: a large crucible (average 400 ml) and a small one (average 50 ml). The iron crucible was charged with hydrous KOH (and/or NaOH), and ZnO reagents of first classes. The crucible containing the charge was not covered with a lid. The crucible was placed in a vertical and Kanthal wire resistance furnace. The experimental arrangement, and the temperature distribution in the furnace, are shown in Fig. 1. ZnO single crystals can grow at growth temperatures ranging from 450–900 °C over 1–120 h. In order to determine the optimum growth conditions, various runs were made at different growth temperatures and times. The crystals grown were removed by dissolving KOH in water.

3. Results

From the results of the titration studies, it was found that 28.5 wt % and 25.4 wt % H_2O was present in

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TABLE I Experimental results for the growth of ZnO single crystals

Crucible size	Run no.	KOH (g)	ZnO (g)	Temp. (°C)	Time (h)	Yield (wt %)	Colour	Max. crystal size (mm)
Small	A-6	5.8	30	450	80	67	Dark brown	Fine crystal
	A-7	5.8	30	480	80	50	Brown, dark brown	4
	A-3	5.8	30	500	1	14	Brown, dark brown	3
	A-4	5.8	30	500	20	47	Brown	7.5
	A-8	5.8	30	500	20	53	Brown, dark brown	6
	A-1	5.8	30	500	80	35	Brown, dark brown	5
	A-9	2.9	15	500	20	75	Brown	2
	A-10	5.8	60	500	80	13	Black	Fine crystal
	A-5	5.8	30	600	20	59	Brown	5
	A-12	5.8	30	800	20	37	Black	Fine crystal
	A-11	5.8	30	800	20	43	White	7
	A-13	11.6	30	800	20	40	Light brown	5
Large	B-1	58	300	500	120	54	Brown	5
	B-2	58	300	800	37	35	Light brown	5
	B-3	58	300	900	30	28	White	8
	B-4	58	(KOH 150) (NaOH 150)	500	72	58	Light brown	18

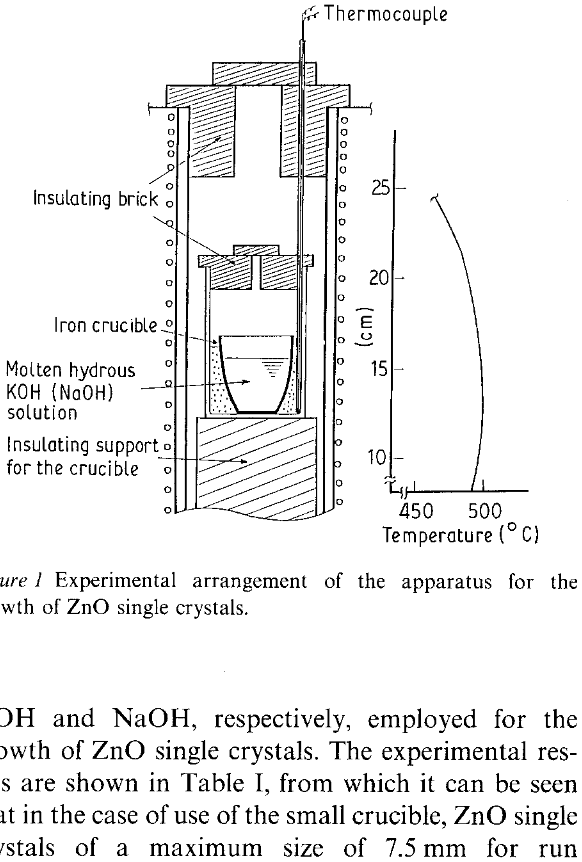


Figure 1 Experimental arrangement of the apparatus for the growth of ZnO single crystals.

KOH and NaOH, respectively, employed for the growth of ZnO single crystals. The experimental results are shown in Table I, from which it can be seen that in the case of use of the small crucible, ZnO single crystals of a maximum size of 7.5 mm for run (A-4) were grown. However, for the large crucible, ZnO single crystals of 18 mm were grown at 500 °C over 72 h (run B-4) with KOH and NaOH fluxes. A cross-sectional drawing of the crucible after the run is shown in Fig. 2. The slender and hexagonal ZnO single crystals had grown at the wall of the crucible, but at bottom of the crucible thick and long ZnO single crystals had grown. The crystals grown in each run are shown in Fig. 3 and scanning electron micrographs for each run are given in Fig. 4. The tops of the hexagonal prisms of the ZnO single crystals were in the shape of hexagonal pyramids.

An enlarged photograph of the top of a ZnO single crystal is shown in Fig. 5. The ZnO single crystal is bounded by both p- and m-faces.

The variation in crystal size normal to the c-face at 500 °C with time is shown in Fig. 6, using a small crucible. After 20 h, crystal growth rates became smaller. The yields of each ZnO crystal size are shown by the black circles in the figure. When using a small crucible, it appears that a growth temperature of 500 °C was the optimum one.

The relationship between crystal size and growth temperature is shown in Fig. 7. For a small crucible, large ZnO single crystals were prepared at 500 °C, but for a large crucible, large ZnO single crystals of 8 mm were synthesized at 900 °C, and further, large ZnO crystals of 18 mm were grown when KOH and NaOH fluxes were used.

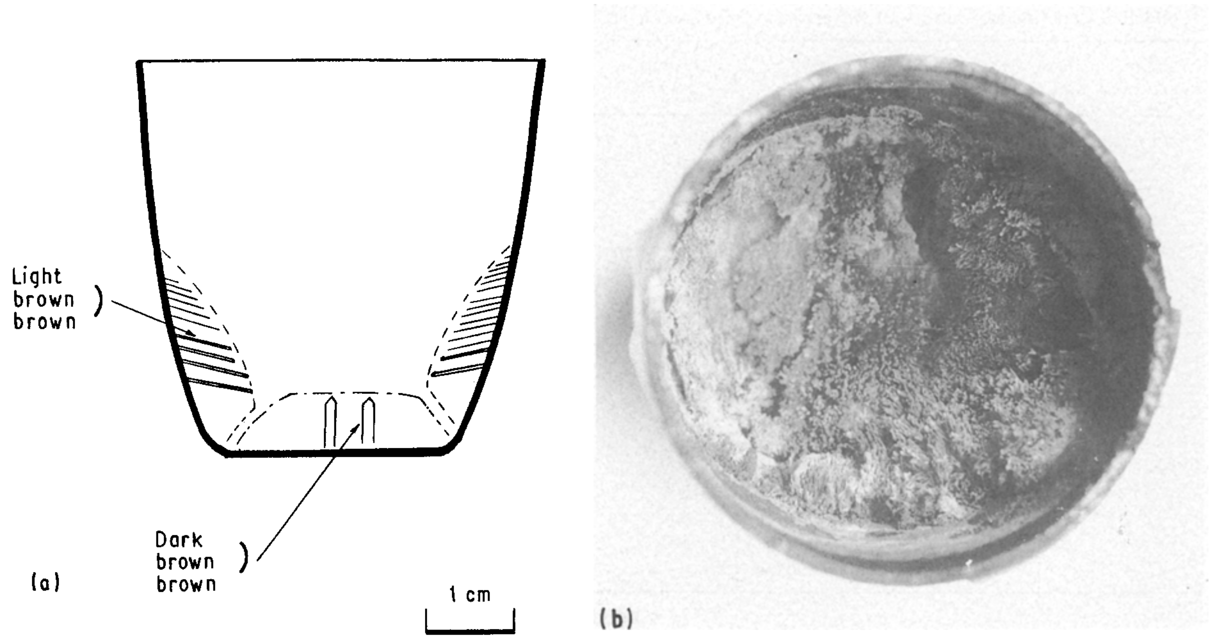
X-ray powder diffraction patterns for each run are shown in Fig. 8. The positions (2θ) of all the peaks except the X-ray intensities, coincided with those of the standard ZnO material [18]. Laue photographs of each run are shown in Fig. 9. For a growth temperature of 800 °C, sharp spots were observed, but the striae of spots were observed at 500 °C.

The amount of evaporation of molten KOH solvent is shown in Fig. 10. For the large crucible, the amount of the evaporation shows a value twice as high as that of the small crucible.

4. Discussion

4.1. Growth of ZnO single crystals

Needle-shaped crystals were observed to grow on the wall and bottom of the crucible at a growth temperature of 500 °C for 20 h, using the small crucible. The crystals were brown in appearance and up to 7.5 mm long and nearly 0.5 mm diameter (Table I and Fig. 7). However, ZnO single crystals, 18 mm long and nearly 1.0 mm diameter were grown when using KOH and NaOH fluxes. These crystals were light brown at 500 °C for 72 h, when the large crucible was used. It appears that the basicity of the NaOH melt was slightly lower than that of KOH, therefore, NaOH was more suitable for the growth of ZnO single crystals, although both KOH and NaOH melts.



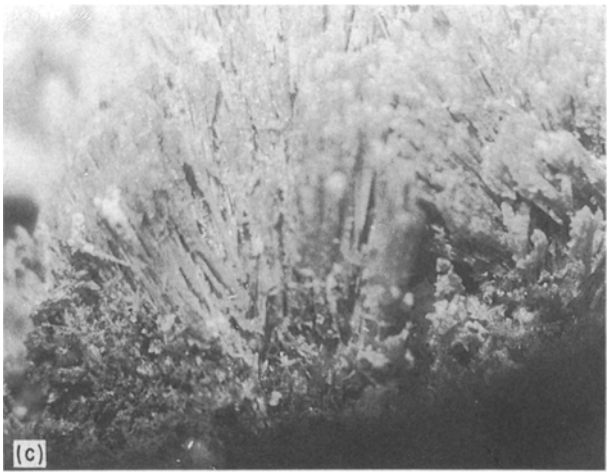


Figure 2 (a) Schematic drawing of the cross-section through a crucible, and (b, c) enlarged photos of crystal groups with diameters about 0.2 mm at 500 °C.

In the grown ZnO single crystals, all side-faces were bounded by m-faces ($\{10\bar{1}0\}$) and showed a hexagonal prism of the first order. The top of the needle-shaped ZnO single crystals was a hexagonal pyramid and bounded by a p-face ($\{10\bar{1}1\}$) (Fig. 5).

From the variation of crystal size normal to the *c*-axis with time (Fig. 6), ZnO single crystals grew relatively rapidly below 20 h, but beyond this the crystals grew very little and the crystal size was nearly constant. It seems that the amount flux melt in the crucible was adequate and crystal growth rates were constant, therefore, crystal growth progressed when the growth time was below 20 h, but the amount flux melts was smaller due to evaporation after 20 h, and crystal growth was late.

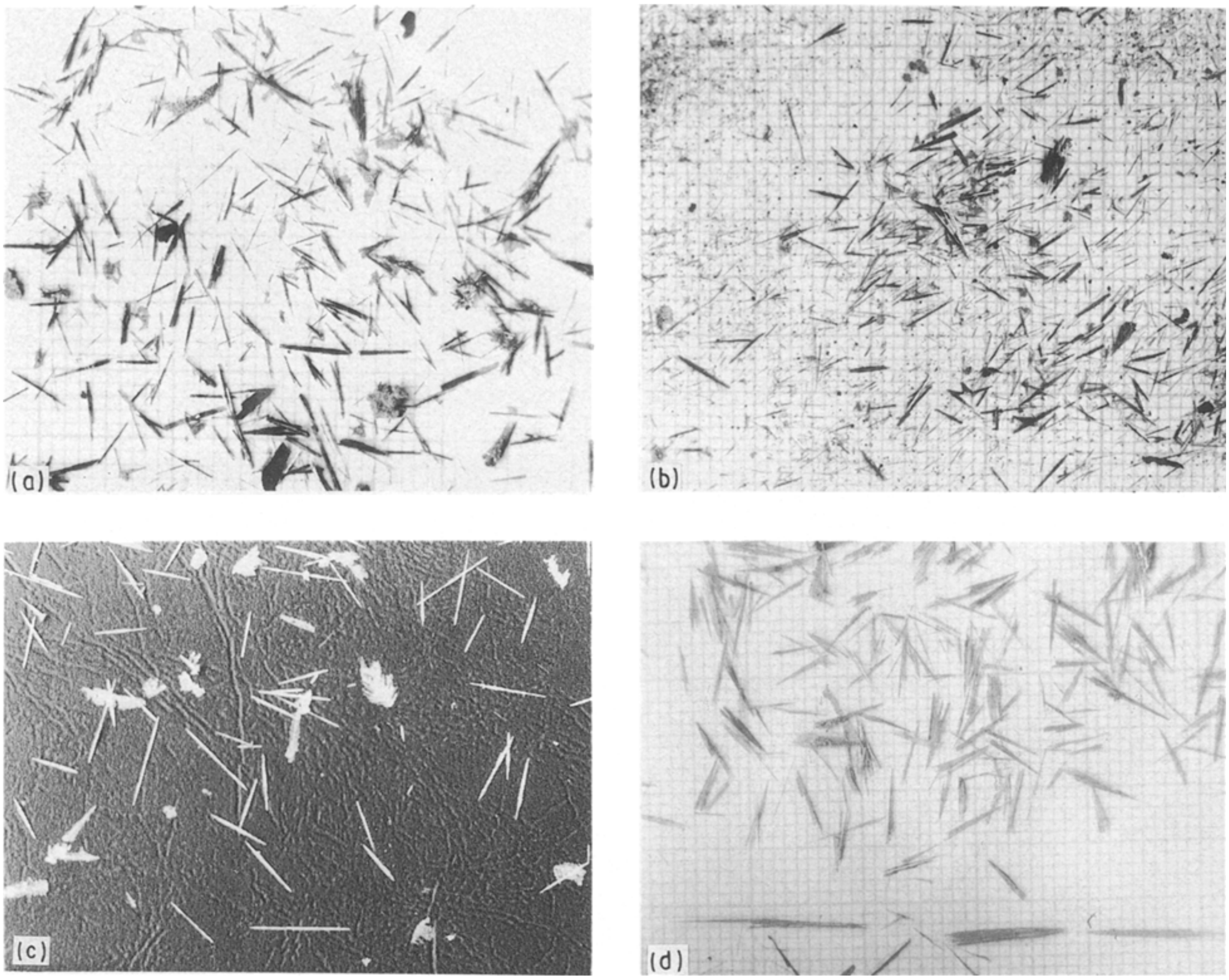
With a small crucible, the maximum sized ZnO single crystals (7.5 mm) were prepared at 500 °C for 20 h and crystals of 7 mm were grown at 800 °C for 20 h. In the latter, it seems that a growth temperature of 800 °C was important because the flux melt evaporated before 20 h had elapsed. The colour of the crystals grown under these conditions became lighter as the growth temperature increased. It is considered that ZnO single crystal could be difficult to contaminate with iron ions as the growth temperature increased, because of a problem of solid solubility at high temperature.

On the other hand, when using the large crucible, ZnO single crystals of 5–8 mm were grown at temperatures ranging from 500–800 °C with KOH melt, but with a KOH–NaOH flux, ZnO crystals of 18 mm were prepared. It may be assumed from the phase diagram of the system KOH–NaOH, that the eutectic temperature is nearly 140 °C, and the decomposition voltage for NaOH is about 2.4 V and that for KOH is a lower value (1.6 V) at 400 °C [19, 20]. In order to contain NaOH in the KOH solution, the evaporation rate of the solvent may be lower than that of KOH solution alone, and it seems that the grown crystals are soaked for a long time, as described above.

4.2. X-ray diffraction patterns

In Fig. 8, the 2 O-positions of all peaks coincide with that of the standard material of ZnO [21]. The relationship between the intensity ratios of (1 0 1) (strong peak)/(1 0 0) (second strong peak) and growth temperature is shown in Fig. 11. Where a double peak shows a ratio of standard material of ZnO [21] and s.m. lattered sign shows the starting material to be ZnO. Below a ratio of 1.0, the degree of ZnO crystallization was inferior to that of the starting material of ZnO at a heat-treatment below 800 °C.

From the results of the Laue photographs normal to the *c*-axis, sharp spots were observed for a growth temperature of 800 °C. It seems that the ZnO single crystals grown had a very good crystallinity. However, the striae of spots were observed for a heat treatment of 500 °C. It may be assumed that either the grown ZnO crystals were gathered together to form a bundle or had the wrong crystallinities.



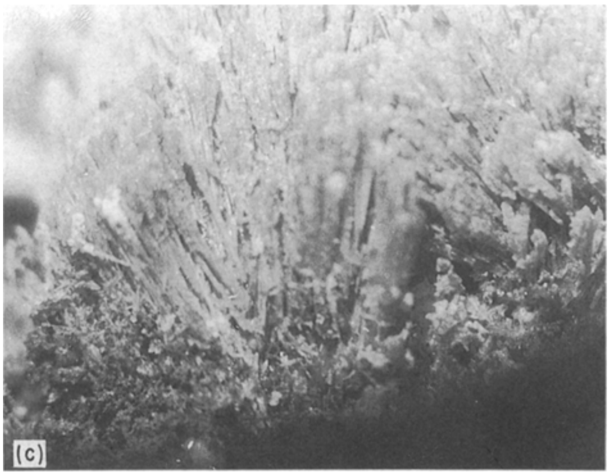


Figure 3 The ZnO single crystals grown for each run. (a) Run A-4, 7.5 mm; (b) Run A-5, 5 mm; (c) Run B-3, 8 mm; (d) Run B-6, 17 mm; (e) Run B-6, 18 mm.

4.3. Number of crystals

Similarly, we developed an equation for the total weight of crystals, W, as follows

$$W = vt$$

$$= \rho \sum_{i=1}^{n} S_j l_i \qquad (1)$$

where ρ is the density of a ZnO crystal (5.606 g cm^{-3}), S is the surface area of a crystal, l the length of a crystal, and v the rate of deposition (g h^{-1}).

If the crystal diameter of 0.2 mm and the length of the crystal as shown in Fig. 6 (large black circle) are considered to be constant, $vt = n\rho Sl$, where n is the number of crystals. Equation 1 can be rewritten

$$n = 51.5\left(\frac{t}{l}\right) \qquad (2)$$

l is constant at each growth temperature as described above. This relation is shown in Fig. 12. The dotted lines show the results from Fig. 6. The number of crystals seems to be 250–300, agreeing approximately with the results of counting the grown crystals.

4.4. Speculation of the formation of ZnO single crystals from the dissociation mechanism of a KOH–ZnO melt

A KOH melt is ionized to K^+ and OH^- [19, 20]

$$KOH \rightarrow K^+ + OH^-$$

OH^- is a strong O^{2-} donor, in accordance with

$$2OH^- \rightarrow H_2O + O^{2-}$$

ZnO is soluble by the formation of a higher complex with O^{2-}

$$ZnO + 2OH^- \rightarrow ZnO_2^{2-} + H_2O$$

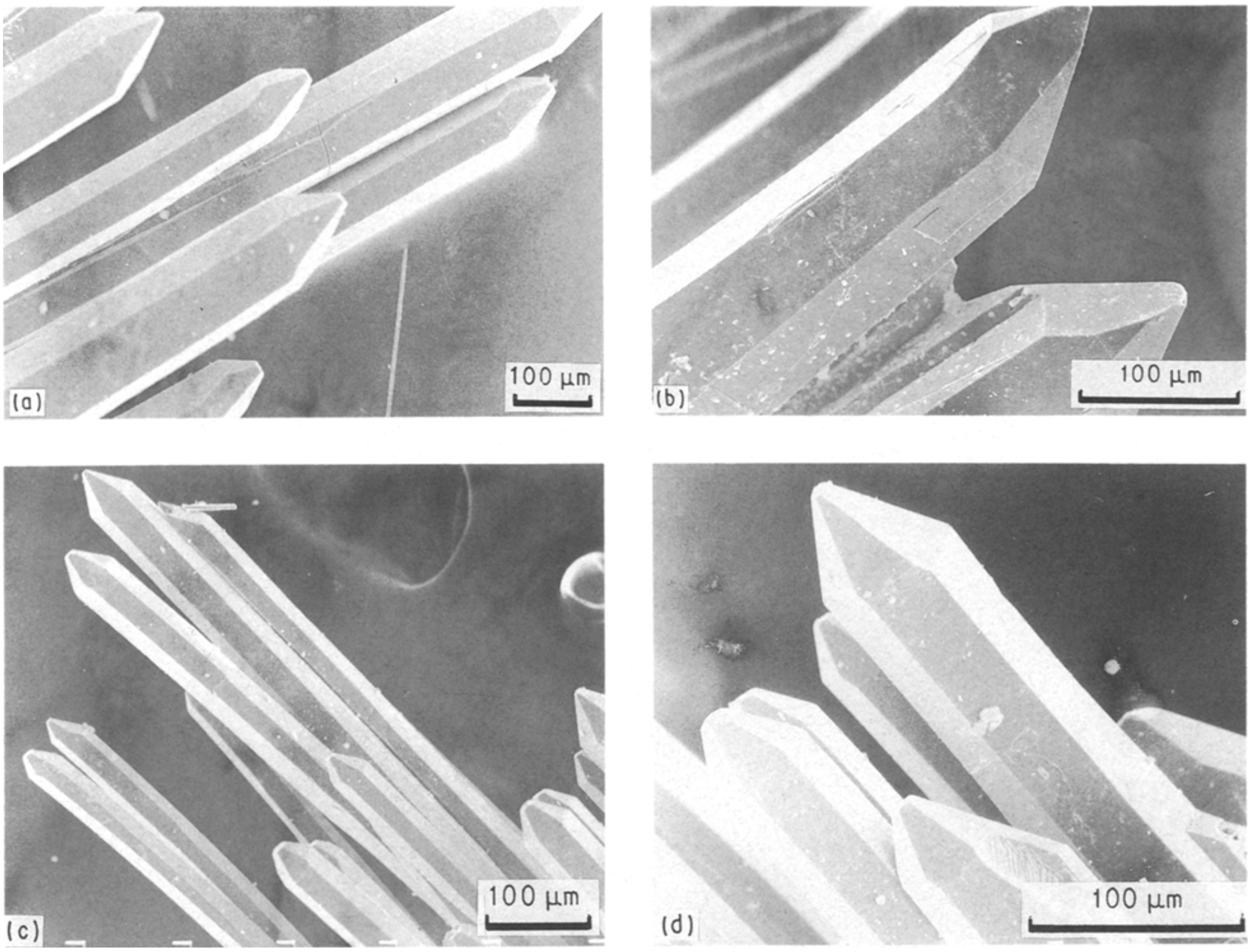


Figure 4 Scanning electron micrographs for each run. (a) Run A-4, (b) Run A-5, (c) Run B-3, (d) Run B-4.

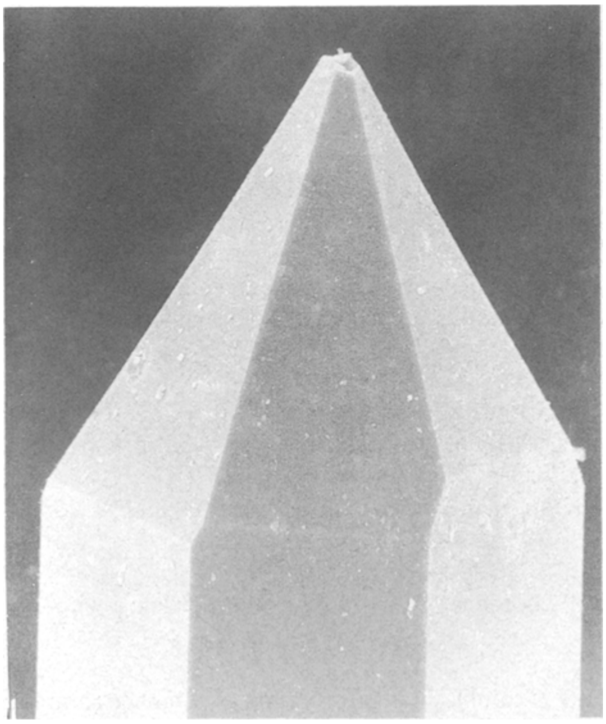
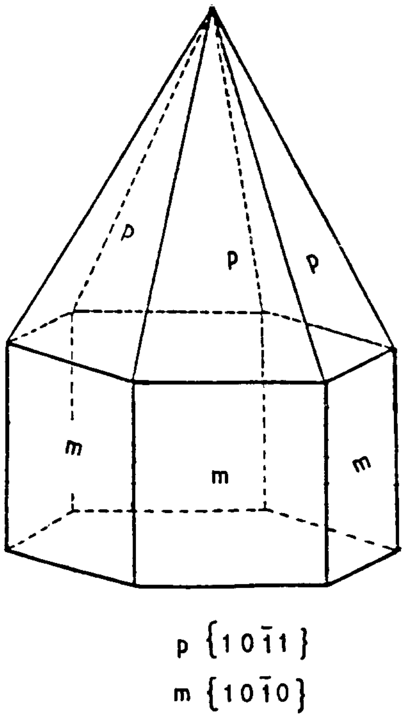


Figure 5 Enlarged photograph of the top of a ZnO single crystal.



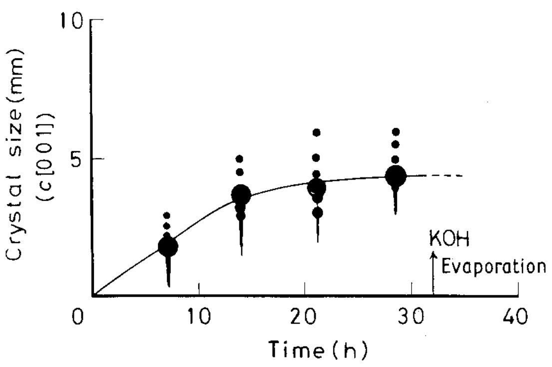


Figure 6 Variation of crystal size with time at 500 °C.

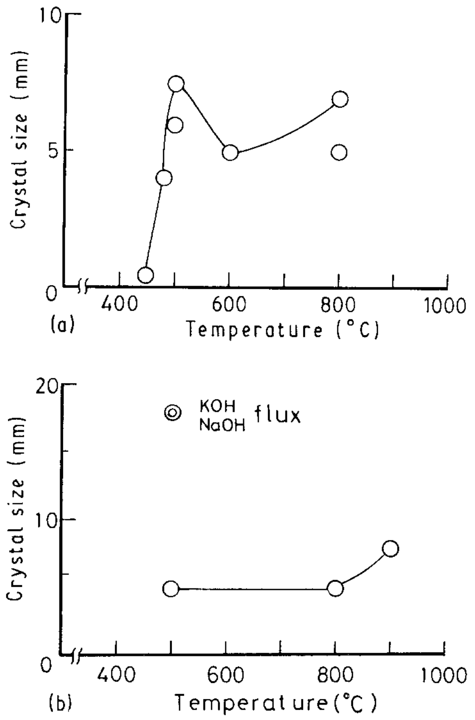


Figure 7 Relationship between crystal size and temperature. (a) Small crucible. (b) Large crucible.

This zincate ion (ZnO_2^{2-}) with linear structure is confirmed from the Laser Raman spectroscopic investigation by Kashayap [18]. The ion is oxidized by

$$ZnO_2^{2-} \rightarrow ZnO + O^{2-}$$

Thus ZnO is formed. The NaOH melt may be assumed to have the same behaviour as the KOH melt.

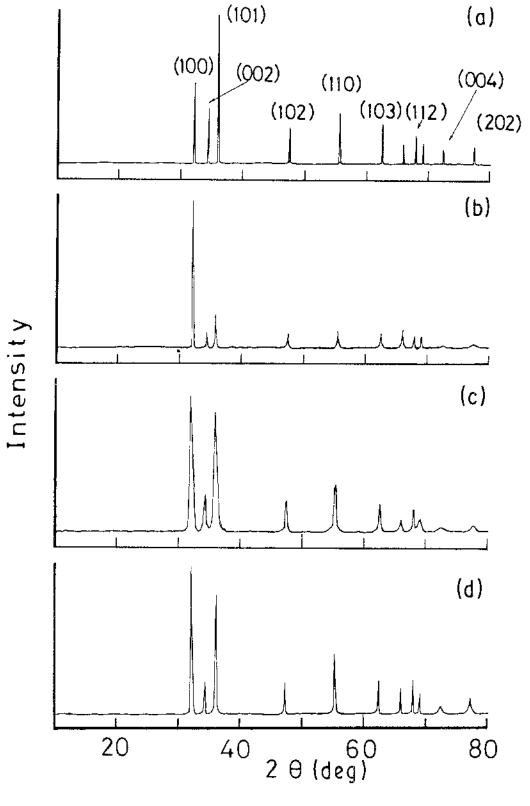


Figure 8 X-ray diffraction patterns for each run: s.m., starting material. (a) s.m. ZnO; (b) A-7, 480 °C, 80 h; (c) A-1, 500 °C, 80 h; (d) A-5, 600 °C, 20 h.

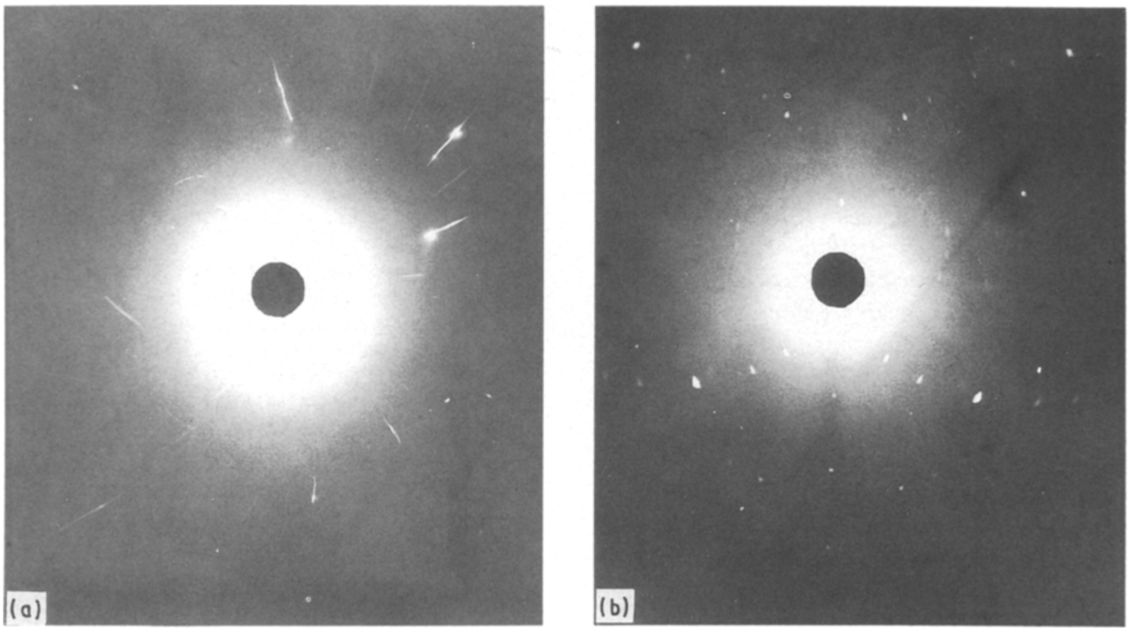


Figure 9 Laue photographs normal to m-face for each run. (a) Run A-4, (b) Run A-11.

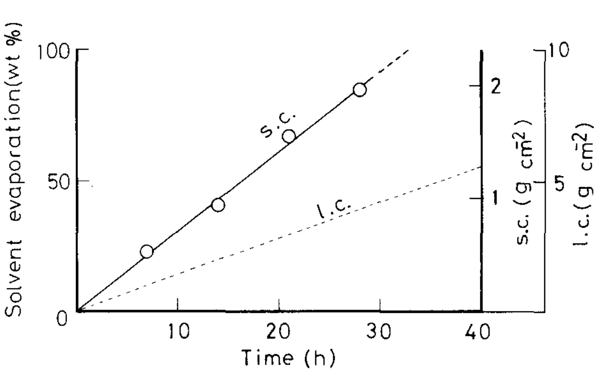


Figure 10 Relationship between evaporated amounts of KOH solvent and growth time at 500 °C: s.c., small crucible l.c., large crucible.

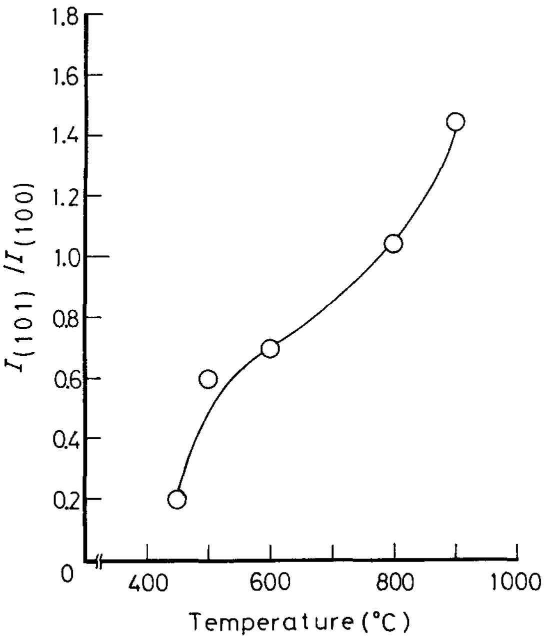


Figure 11 Relationship between degree of crystallization and growth temperatures: (○) starting material, (◎) ASTM card 5–664.

4. Conclusions

Based on this study on the growth of ZnO single crystals at 450–900 °C and for 1–12 h, using hydrous KOH and NaOH melts as fluxes, the following conclusions can be drawn.

1. When using only the KOH flux, brown ZnO single crystals with a maximum dimension of 0.5 mm diameter × 7.5 mm were grown at 500 °C for 20 h and white crystals of 0.5 mm diameter × 7 mm were grown at 800 °C for 20 h, using a 50 ml crucible.

2. When a 400 ml crucible was used, ZnO single crystals with 0.5 mm diameter × 8 mm were formed at 900 °C for 30 h. However, using a KOH + NaOH (1:1) flux, light-brown crystals of largest diameter 1.0 mm × 18 mm could be grown.

3. The ZnO single crystals grown are bounded by both p- and m-faces.

4. Crystal qualities were high when crystals were grown under conditions of 900 °C for 30 h, but the qualities were low as the growth proceeded at 500 °C.

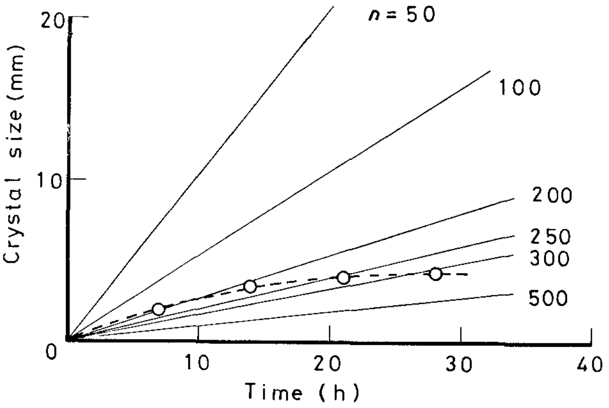


Figure 12 Number of crystals grown, calculated from Equation 2.

5. The formation mechanism of ZnO single crystals from KOH (or NaOH) + ZnO melt was estimated to follow a course of dissociation and formation of ZnO single crystals

$$\mathrm{KOH} \rightarrow \mathrm{K}^{+} + \mathrm{OH}^{-}$$

$$\mathrm{ZnO} + 2\,\mathrm{OH}^{-} \rightarrow \mathrm{ZnO}_2^{2-} + \mathrm{H_2O}$$

$$\mathrm{ZnO}_2^{2-} \rightarrow \mathrm{ZnO} + \mathrm{O}^{2-}$$

The NaOH melt may exhibit the same behaviour with the KOH melt.

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