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Effect of electric field on the growth of barium molybdate crystals in silica gel

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The growth of $BaMoO_4$ crystals in silica gel under the influence of an externally applied uniform electric field is studied. The habit changes resulting from different growth parameters are reported. Crystals up to 4.0 mm × 1.2 mm × 0.9 mm were obtained under field. The morphology of some crystals is examined by optical and scanning electron microscopy.

1. Introduction

Barium molybdate has the tetragonal scheelite structure [1]. It has been the subject of acoustic, optic, laser [2] and electronic studies [3], and the crystals have been grown by Czochralski [4], hydrothermal [5] and gel [6, 7] methods. Single crystals grown in silica gel media are faceted, octahedral bipyramids, but the drawback of this method is its slow growth rate [8]. Magnetic and electric fields have been used in liquid–solid growth [9] and theory of accelerated diffusion under constant electric field has been developed by Mysels [10] Lamm [11] and Simnad and Ling Yang [12]. In this paper we report the effect of electric field on the growth of $BaMoO_4$ crystals in silica gel.

2. Experimental procedure and results

The apparatus consists of an electrolytic cell of length 12 cm and diameter 2.5 cm (Fig. 1). A suitable d.c. voltage is applied between two carbon electrodes, acting as anode and cathode. Current in the circuit is recorded by means of a sensitive milliammeter (mA).

The following variables were investigated: (1) pH of the gel medium, (2) concentration of reagents, (3) age of gel, and (4) polarity of applied voltage.

2.1. Variation of concentration of top solution for the same pH value

The two growth systems (as shown in Figs. 2 and 3) were filled with a gel mixture containing equal volumes of sodium silicate solution of 1.03 density and 0.001 M ammonium molybdate solution. The pH was adjusted to 6. While plugging the rubber corks after pouring 0.2 M, 0.15 M, and 0.1 M $Ba(NO_3)_2$ solution, care was taken to ensure that no air bubbles existed between the electrode and the solution.

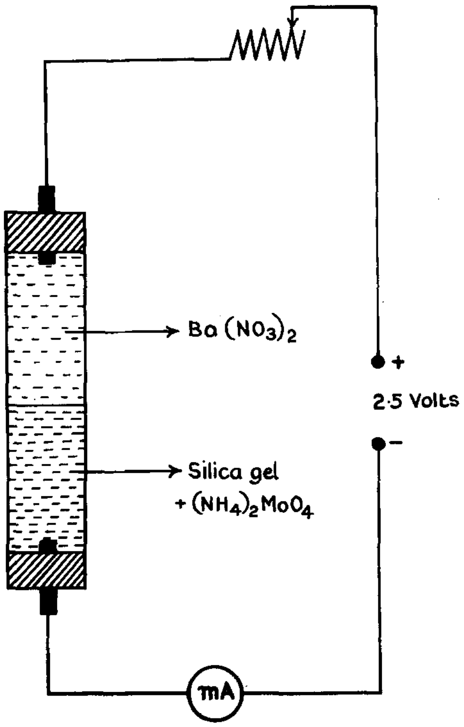

Figure 1 Schematic diagram of the electrolytic cell.

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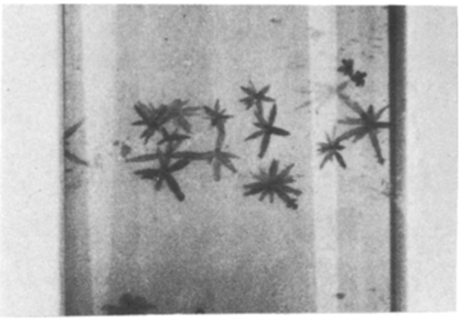

Figure 2 Accentuated growth of $BaMoO_4$ crystals under electric field.

After 1½ to 2 h, a large number of nucleation centres of polycrystalline aggregates began to appear just below the gel interface, after forming a small white precipitate column. This stage took 10 to 12 h for completion. After 10 h, the nucleation shifted towards the cathode, each nucleation centre at its rudimentary stage consisting of a set of octahedral crystals hinged to a common centre (Figs. 2 and 4). As time elapsed the length (*d* mm) of the individual arms of star-shaped crystals were subjected to a kind of accentuated growth with an average rate of nearly 1.5 mm day^{-1}, ultimately attaining a dagger shape (Figs. 5 and 6). The growth rate and final length of each arm was greater for low concentrations of top solution (Fig 7), although the number of nucleation centres was lower. A high current recorded immediately after the onset of the experiment, was found to dwindle exponentially (Fig. 8) with time. After 6 to 7 days, the current became practically nil, by which time the crystallization in both zones was almost complete.

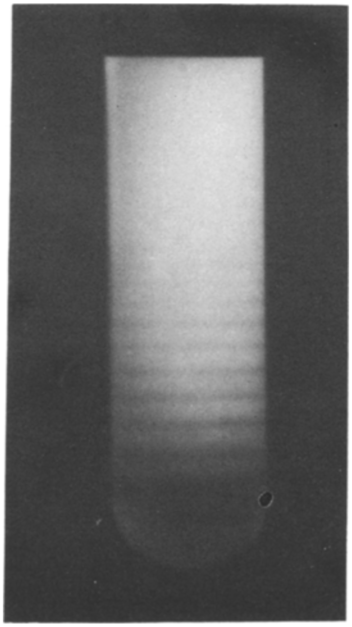

Figure 3 Liesegang ring formation without field.

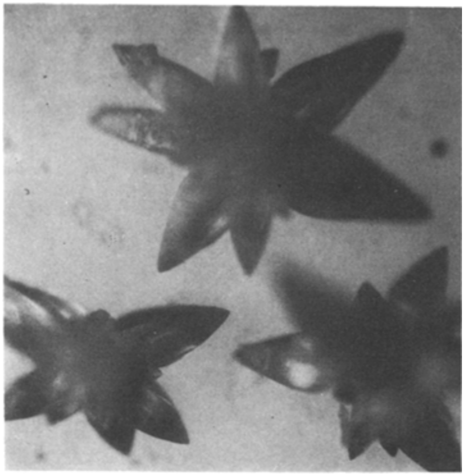

Figure 4 Radiant star-like growth of $BaMoO_4$ crystals in its rudimentary stage, × 18.75.

In the second system (Fig. 3) "Liesegang rings" [13] were obtained on account of spontaneous crystallization of molecules obeying the "time law" [14], and the "spacing law" [15]. At the top, the precipitation was continuous but soon bands (Fig. 3) separated by relatively clear spaces were produced.

The results obtained are given in Table I.

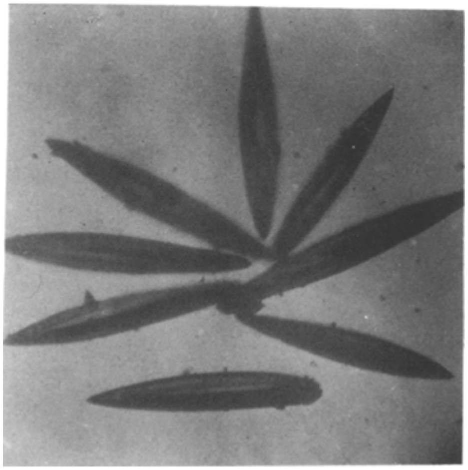

Figure 5 Fully grown dagger-type octahedral needles, × 18.75.

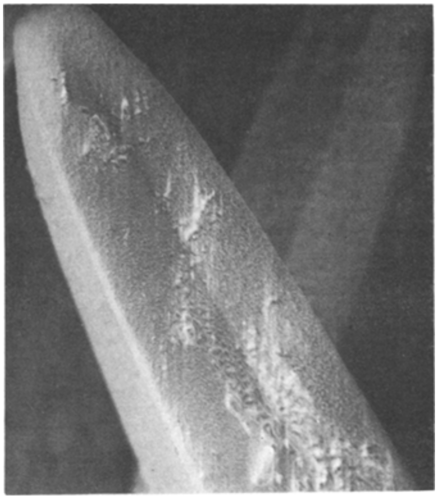

Figure 6 Enlarged SEM view of fully grown octahedral needle, × 150.

2.2. Variation of pH of gel Media

Keeping the pH of gel medium at 7.5, all the remaining growth parameters were kept unaltered. Precipitation occurred below the gel interface, in all cells after the onset of the experiment, the rate being directly proportional to the concentration of the top solution. For 0.2 M top solution, one Liesegang ring was also formed. As time elapsed some dendritic nucleations originated just below the ring (Fig. 9). The main stem of the dendrite was found to grow downwards, with side branchings of nearly 60° inclination and terminated with enumerable number of octahedrons (Fig. 10). The same type of growth was found below the precipitation column in the case of 0.15 M and 0.1 M systems, but devoid of Liesegang ring formation. After 6 to 7 days the growth mechanism of the

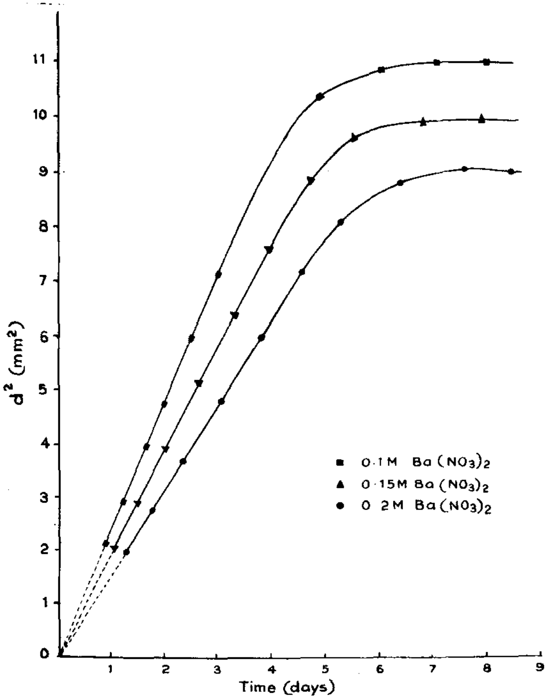

Figure 7 Parabolic growth curves representing accentuated growth under electric field.

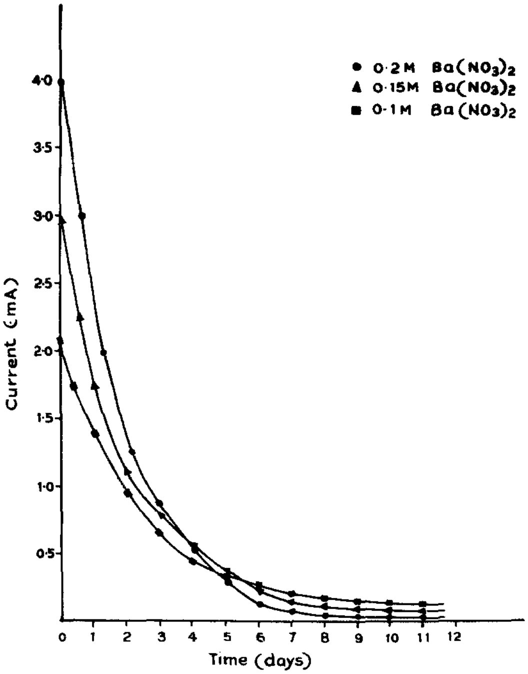

Figure 8 Exponential decay of current in the gel medium.

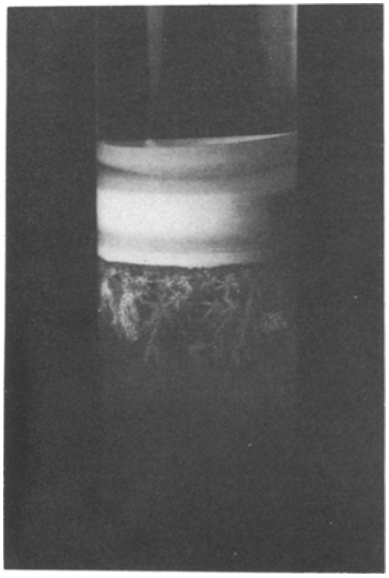

Figure 9 Growth system under electric field for enhanced pH (7.5) leading to dendritic growth.

TABLE I

Growth system	Polarity	pH	Age of gel	Concentration of top solution $Ba(NO_3)_2$ (M)	Nature of crystallization	Crystallization time (h)	No. of crystals	Maximum size (mm × mm × mm)
With field	Electrode touching top solution is at +ve potential	6	24 h	0.2	Star-shaped centres; the individual branches later assume dagger shape	130	30	2.8 × 0.5 × 0.3
		6	24 h	0.15		120	20	3.5 × 0.8 × 0.5
		6	24 h	0.1		110	14	4.0 × 1.1 × 0.9
	Reversing the polarity	6	24 h	0.2	Dendrites octahedrons and twinned forms	2	Innumerable	–
		6	24 h	0.15		2.5		–
		6	24 h	0.1		3		–
Without field		6	24 h	0.2	Periodic precipitation of microcrystals in the form of bands	125	Uncountably large	Nuclei very small; measurement not feasible
		6	24 h	0.15		130		
		6	24 h	0.1		175		

Figure 10 Enlarged SEM view of top of a dendrite, × 150.

whole system came to a standstill and the current in the circuit became practically nil.

In the control tubes without field, well faceted octahedral bipyramidals (Fig. 11) were obtained throughout the length of the tube. The length (d mm) of them along the z-axis was found to obey the parabolic relation of growth (Fig. 12).

2.3. Variation of age of gel

Maintaining a suitable pH value between 7 and 8, gels of different ages, 48, 72 and 96 h, were selected. On application of electric field a single growth-front region was formed below the gel interface. The crystals nucleated were mainly octahedral bipyramids, cruciform twins, interpenetrated twins, etc. It took 8 to 10 h for completion of growth. However, in control tubes, both precipitation and microcrystals were obtained within 15 to 20 days.

Figure 11 Octahedral bipyramid $BaMoO_4$ crystals nucleated in control tubes without electric field, × 300.

3. Discussion

Under electric field Ba^{2+} and MoO_4^{2-} ions move in opposite directions, and Ba^{2+} ions are repelled from the anode. A chemical inhomogenity thus produced in the medium changes the structure and nature of the growth system. In other words, an anisotropic effect in diffusion is produced under electric field [16]. The theory of diffusion of Simnad and Ling Yang [12], Lamm [11], Mysels [10, 17] and Kauman [18] anticipates an accelerated diffusion given $D_e = D_0 + U^2E/2K$ where U is the product of ionic mobility and charge, E the intensity of the field and K a rate constant. Ba^{2+} and MoO_4^{2-} ions drift in opposite directions under electric field and a supersaturated metastable state region is formed just below the interface which ultimately leads to the crystallization of twinned crystals, and polycrystalline aggregates. Meanwhile, some of the Ba^{2+} ions escape through this crystallization front and reach the cathode region, where a moderately supersaturated region is created. The accentuated growth of octahedral crystals along the z-axis, being perpendicular to an equatorial plane of symmetry, takes place due to the effect of the field. This is attributed to the anisotropic interfacial free energy as well as anisotropic rate constant [19].

The gel medium as such exerts a kind of frictional force to the ionic motion on account of its viscosity and structure. For alkaline and older gels, ionic velocity is small. With diminishing acidity the cellular nature of the gel becomes less distinct [20]. It is also plausible to conclude that the decrease in current is due to age of the gel. Ba^{2+} and MoO_4^{2-} ions under an electric field drift in opposite directions and a supersaturated metastable state is formed just below the gel interface. The ionic velocity is therefore accelerated to a value adequate for the formation of well-shaped twinned crystals and dendrites. Again for slightly high concentrations of top solution the condition for the formation of Liesegang ring $C_A = C_B$ [21] is satisfied. Subsequently the supersaturated region created below the ring leads to the formation of dendritic growth. Dendrites propagate through the supersaturated region at maximum possible velocity consistent with the constraint. Application of an electric field pro-

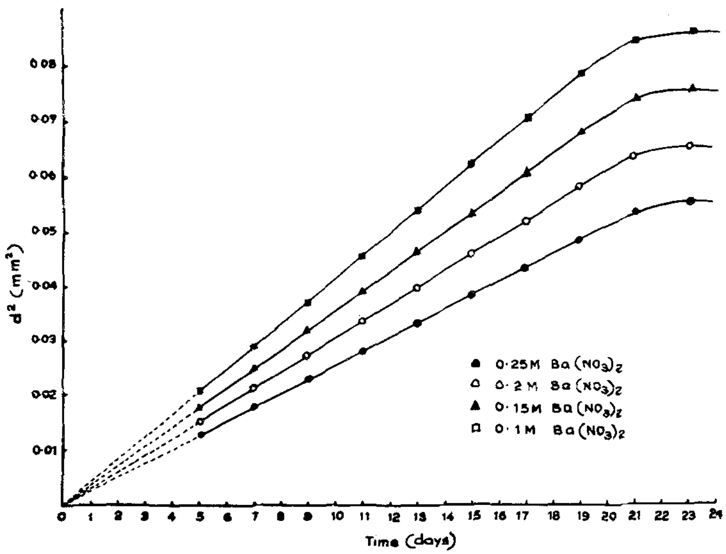

Figure 12 Parabolic growth curves representing growth of BaMoO$_4$ crystals in control tubes without electric field.

moted linear growth along the *z*-axis perpendicular to the equatorial plane of symmetry, and side branching is conjectured as being due to the accentuated growth of [1 1 1] and [1 1 $\bar{1}$] sides of a tetragonal bipyramid coming under the scheelite group [1]. In all cases the exponential decay in current observed is assumed to be due to the joining of Ba^{2+} and MoO$_4^{2-}$ ions for crystallization and the current value becomes zero when crystallization is complete.

4. Conclusions

It has been found that an electric field affects the growth of BaMoO$_4$ crystals in silica gel media in the following ways:

(1) the crystals take less time to attain maximum size;

(2) a tremendous increase in size of the crystal leading to an easily perceptible and measurable quantity, is observed;

(3) a suitable and definite control over growth rate and nucleation centre formation is exercised.

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References

1. HENRY A. MIERS, "An introduction to scientific study of minerals" (Macmillan, New York, 1902) pp. 218, 548, 560.
2. YU. G. PETROSYAN, E. V. TKACHENKO and ZHUKOVSKI, *Inorg. Mater.* **11** (1975) 1381.
3. "The Condensed Chemical Dictionary", 8th Edn. (Van Nostrand Reinhold, New York, 1971).
4. TU CHEN, *J. Crystal Growth* **20** (1973) 29.
5. B. N. LITVIN, L. N. DEMYANETS, L. S. GARSHINA. in "Growth of crystals", Vol. 4, edited by A. V. Shubnikov and N. N. Sheftal (Consultants Bureau, New York, 1966) p. 134.
6. S. A. CHO, J. A. GOMEZ, R. CAMISOTTI and J. C. OHEP, *J. Mater. Sci.* **12** (1977) 816.
7. K. V. KURIEN and M. A. ITTYACHEN, *J. Crystal Growth* **47** (1979) 743.
8. H. K. HENISCH, "Crystal Growth in Gels", (Pennsylvania State University Press, Pennsylvania, 1970).
9. R. A. LAUDISE, "Crystal Growth, Proceedings of an Internation Conference on Crystal Growth", Boston, USA, edited by H. Steffen Peiser (Pergamon Press, New York, 1966) p. 3.
10. K. J. MYSELS, *J. Chem. Phys.* **24** (1956) 371.
11. O. LAMM, *Acta. Chem. Scand.* **10** (1956) 1132.
12. M. SIMNAD and LING YANG, *J. Chem. Phys.* **23** (1955) 1296.
13. R. E. LIESEGANG, *Phys. Chem.* **23** (1897) 365.
14. H. W. MORCE and U. G. W. PIERCE, *ibid.* **45** (1903) 589.
15. K. JABLCZYNSKI, *Bull. Soc. Chim. France.* **33** (1923) 1952.
16. H. J. ARNIKAR, *Nature* **194** (1962) 271.
17. K. J. MYSELS and P. C. SCHOLTEN, *Trans. Faraday Soc.* 57 (1961) 764.
18. W. G. KAUMAN and T. A. BACK, *ibid.* **55** (1959) 1109.
19. S. O'HARA, L. A. TARSHIS, W. A. TILLER and J. P. HUNT, *J. Crystal Growth* **3, 4** (1968) 555.
20. H. S. HALBERSTADT, H. K. HENISCH, J. NICKEL and E. W. WHITE, *J. Colloid and Interface Sci.* **29** (1969) 469.
21. G. K. KIROV, *J. Crystal Growth* **15** (1972) 102.

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