

Crystallization of mixed rare earth (didymium) molybdates in silica gel

SANJAY PANDITA, RAVENDER TICKOO, K K BAMZAI, P N KOTRU* and NEERA SAHNI†

Department of Physics, University of Jammu, Jammu 180 006, India

†Department of Geology, Panjab University, Chandigarh 160 014, India

MS received 3 July 2000; revised 2 May 2001

Abstract. Experiments on the growth of mixed rare earth (didymium—a combination of La, Nd, Pr and Sm) molybdates in silica gel medium are reported. The optimum conditions conducive for the growth of these crystals are described and discussed. Concentration programming is reported to enhance the size of crystals by two-fold; the maximum size obtained being about 1 mm³. EDAX results suggest the crystals to be heptamolybdates of type R₂Mo₇O₂₄, bearing composition La_{1.23}Nd_{0.43}Pr_{0.29}Sm_{0.05}Mo₇O₂₄. The didymium molybdate crystals assume morphologies corresponding to those of spherulites, platelets, cuboids and coalesced crystals. Twinned structure in didymium molybdate crystals are also reported. It is explained that spherulitic morphologies result from aggregates of crystals joining in a spherical envelope. It is suggested that the crystals of didymium molybdates grow by two-dimensional spreading and piling up of layers.

Keywords. Crystal growth; didymium molybdate; gel method; morphology; EDAX.

1. Introduction

Growth of mixed crystals is interesting because their characteristics change from those of the crystals of single components grown separately. For example, mixed crystals are found to be harder than pure ones (Dharma Prakash and Rao 1987; Kotru *et al* 1989a). Large variations in the hardness of pure and mixed KBr and KI system are reported (Subba Rao and Babu 1978, 1980). Gits *et al* (1985) reported doping effect on the quality of ADP when the same was doped with chromium. The effect of doping on gel grown crystals was investigated by Dishovsky and MLadenova (1981) and Dennis and Henisch (1967). Significant changes in physico-chemical characteristics of mixed crystals as brought about in comparison with those of the pure ones were reported in other cases as well (Belikova and Belyaev 1962; Klevtsov *et al* 1975; Kotru *et al* 1989b). Growth of mixed crystals by gel method was reported by Patel and Arora (1977a, b), Wiktorowska *et al* (1983), Kotru and Raina (1986) and Jain *et al* (1996). Growth of neodymium–lanthanum heptamolybdate crystals in silica gels was reported by Bhat *et al* (1995). Rare earth molybdates, in general, have the potential of wide application in science and technology on account of the fact that they exhibit interesting fluorescent, laser, piezoelectric, ferroelectric and ferroelastic properties. Rare earth molybdates are

accepted as being ferroelectric (Borchardt and Bierstedt 1996). We have succeeded in growing single crystals of praseodymium molybdate in silica gels in our laboratory (Pandita *et al* 1998).

In this paper we report a method of growing mixed rare earth (didymium) molybdate crystals at room temperature by encapsulating the suitable reactants in a suitable network employing the gel method. The method involves the growth of didymium (a mixture of La, Nd, Pr and Sm) molybdate crystals by controlled diffusion of chemical reagents through the medium of silica gel. The gel medium provides a three-dimensional structure in which the crystal nuclei are directly held in position for their formation and development, without generating convection currents and turbulence and by maintaining chemical inertness. A literature survey unfolds that no work has so far been reported on the growth of mixed crystals of La, Nd, Pr and Sm (didymium) molybdates in sodium silicate gels at room temperature. The work was undertaken to obtain single crystals of mixed rare earth molybdates for scientific investigations leading to an understanding of their characteristic properties, including dielectric, mechanical, structural and thermal. In this paper the results of experiments on crystallization of didymium molybdate is presented.

2. Experimental

A single tube of dimensions 2.5 cm diameter and 20 cm length, with ~ 75% of its volume filled by one type of

*Author for correspondence

reactant (called 'lower reactant' (LR)) encapsulated in the silica gel network and ~ 25% filled up with the other reactant (didymium chloride) (known as the upper reactant (UR)), was used as a crystallizer as schematically shown in figure 1.

The process of preparation was as follows: 284.20 g of $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ was dissolved in 1 l of distilled water in order to obtain a solution of concentration 1 M. The solution was left undisturbed for a few days and a clear solution was obtained on decantation. The second solution of lower reactant was prepared by adding ammonium molybdate and ammonium nitrate, each weighing 10 g, to 65 cc of distilled water. This solution was thoroughly mixed with a magnetic stirrer and then 30 cc of conc. HNO_3 was added to it drop by drop till a white precipitate was formed. At this stage 30 cc of distilled water was added in order to obtain 125 cc of lower reactant of 0.06 M. The first solution (sodium metasilicate solution) was then mixed with the second solution (lower reactant—a source of molybdenum ions) in the crystallizer. The combined solution of the desired pH was allowed to set in the crystallizer and then aged for the desired time. In our experiments we used gels of ages 24, 48, 72 h or even more. After the gel was set and aged, the upper reactant of a desired molarity was poured along the sides of the tube, ensuring that this process does not break the gel. All experiments were conducted at room temperature of about 25°C . Figure 2 represents the growth of didymium molybdate crystals in a crystallizer. The crystals were examined under optical microscopes, Epignost (for rapid visual examination) and metallurgical microscope (Neophot-2), of Carl Zeiss, Germany and scanning electron

microscope (model JEOL JSM-25 S) coupled with the EDAX system model KEVEX Delta Class. Before examination under the SEM, the crystals were coated with gold by ion-sputter coater model JFC-1100 (JEOL) in order to provide even granularity and efficient high reproducibility.

3. Results and discussion

In order to establish optimum conditions conducive for the growth of mixed rare earth didymium molybdates in the form of single crystals of size suitable for scientific studies, experiments were performed under different conditions of growth parameters including gel concentration, gel pH, concentration of upper and lower reactants and gel ageing. Table 1 provides summary of various details of the experiments and the results obtained. The main conclusion of these experiments was that the optimum conditions for the growth of better size and quality of crystals are gel pH 4.5; UR concentration, 0.25 M; LR concentration (preparation of ammonium paramolybdate, ammonium nitrate and nitric acid), 0.03 M; gel ageing, 72 h and gel concentration, 0.25 M. In an effort to grow crystals of size bigger than what was obtained from the above optimum conditions, experiments on concentration

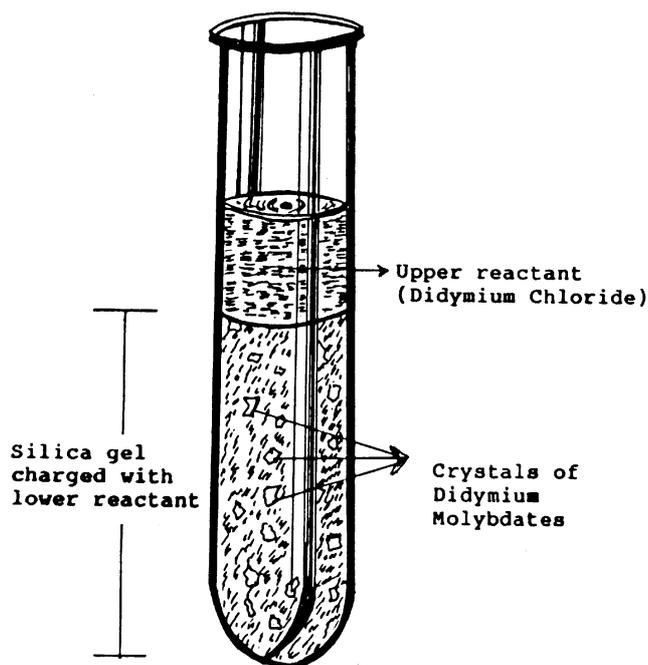


Figure 1. Schematic diagram of a crystallizer.



Figure 2. Growth of didymium molybdate in a crystallizer.

Table 1. Details of experiments used for the growth of didymium molybdate crystals.

Experiment	Constant parameters	Changing parameters	Results
Variation of gel ageing	UR conc. (0.25 M) LR conc. (0.03 M) Gel pH (4.5) Gel conc. (0.5 M)	Gel ageing (24, 48, 72, 96, 144 h)	(i) Morphology: single crystal platelets, spherulites, irregular shaped, hexagonal and crystal aggregates (ii) Nucleation density: min and max at 24 h and 96 h of gel age respectively (iii) Liesegang ring formation at 144 h (iv) Crystallization at all ages
Variation of pH	UR conc. (0.25 M) LR conc. (0.03 M) Gel age 72 h Gel conc. (0.5 M)	Gel pH (4, 4.5, 5, 5.5, 6, 6.5)	(i) Morphology: same as above (ii) Nucleation density: min and max at 5 and 4.5 gel pH respectively (iii) pH values < 4 and > 6 not conducive for crystal growth (iv) Liesegang ring formation at pH 5.5
Variation of LR	UR conc. (0.25 M) Gel age 72 h Gel pH (4.5) Gel conc. (0.5 M)	LR conc. (0.015, 0.03, 0.06 M)	(i) Morphology: same as above (ii) Nucleation density: min and max at 0.015 M and 0.06 M of LR respectively (iii) Crystals nucleate at all LR conc.
Variation of UR	LR conc. (0.06 M) Gel age 72 h Gel pH (4.5) Gel conc. (0.5 M)	UR conc. (0.25, 0.5, 0.75, 1 M)	(i) Morphology: same as above (ii) Nucleation density: min and max at 0.5 M and 0.25 M of UR respectively (iii) Isolated nuclei formed at 0.25 M of UR conc. (iv) Crystals nucleate at all UR conc.
Variation of gel conc.	UR conc. (0.5 M) Gel age 72 h Gel pH (4.5) LR conc. (0.03 M)	Gel conc. (0.125, 0.25, 0.5 M)	(i) Morphology: same as above (ii) Nucleation density: min and max at 0.25 M and 0.5 M of gel conc. respectively (iii) Bigger crystal size at 0.025 M (iv) Crystals nucleate at all gel conc.

Abbreviations used: Upper reactant (didymium chloride) (UR); lower reactant (gel charged with ammonium molybdate and ammonium nitrate) (LR); dimensions of crystallizer and gel column in all experiments are 2.5 cm dia and 20 cm ht and 13 cm respectively.

programming were performed. In such experiments, 0.5 M of upper reactant was poured initially over gel (gel concentration 0.5 M and gel age 72 h) charged with lower reactant (ammonium molybdate and ammonium nitrate) of conc. 0.6 M. After every 144 h, the upper reactant was drained off by a dropper and replaced by upper reactant of higher concentration of molarities viz. 1 M, 1.5 M, 2 M, 2.5 M, 3 M, 3.5 M and 4 M, each time keeping all other growth parameters constant. It was observed that concentration programming led to crystals of increased size, enhancing the ultimate size to 1 mm³ which is more than double the maximum size obtained by normal methods of growth. It was further observed that concentration pro-

gramming only influenced the size but not the morphology of the crystals. It takes about one month for the crystals to grow to the maximum possible size, whether the experiments are performed under normal process of growth or concentration programming. In order to verify if the starting composition and the consequent reaction through diffusion, as controlled by the silica gel, yields crystals of the expected composition, both the starting composition of UR as well as the crystals were examined by EDAX. Figures 3 and 4 show the EDAX patterns obtained from the UR (didymium chloride) and the crystals respectively. The EDAX of figure 3 clearly shows that the upper reactant (didymium chloride (UR)) does

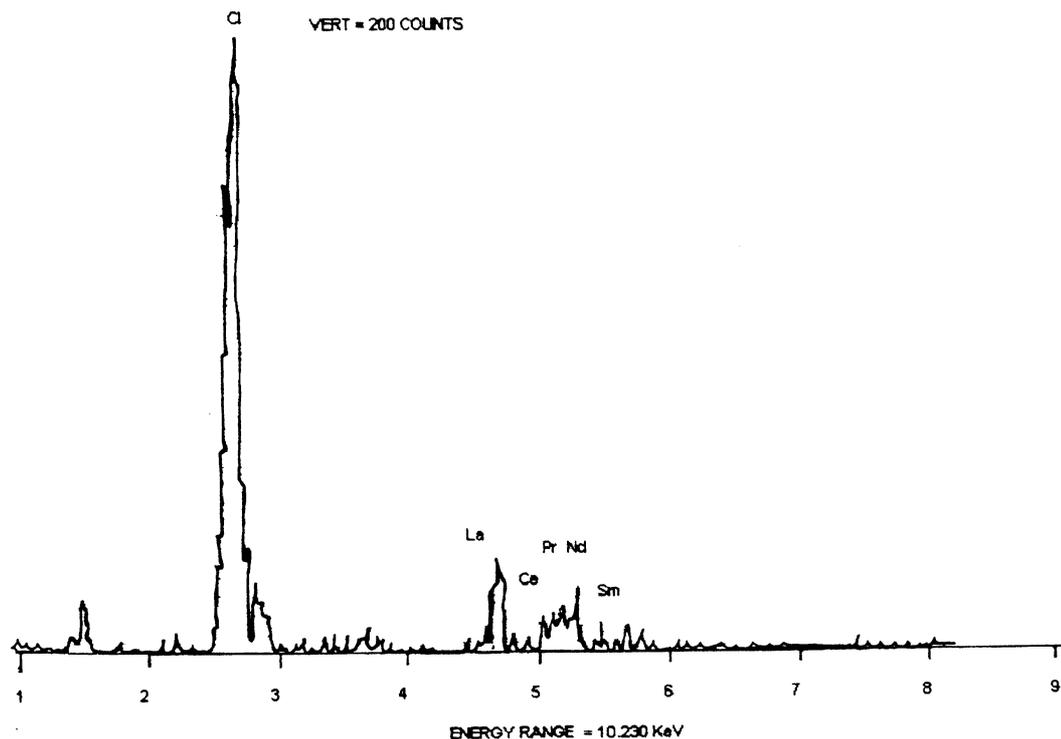


Figure 3. EDAX of starting composition (didymium chloride).

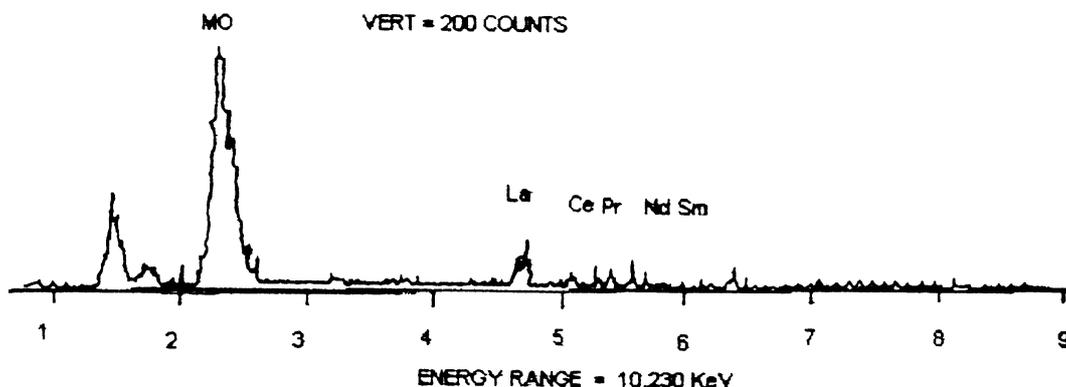


Figure 4. EDAX of didymium molybdate showing peaks corresponding to expected elements Mo, La, Pr, Nd and Sm.

Table 2. Data from EDAX analysis of starting material (didymium chloride).

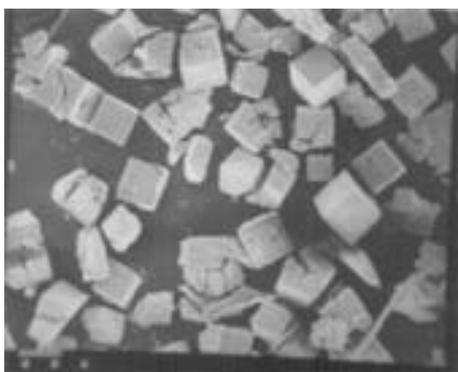
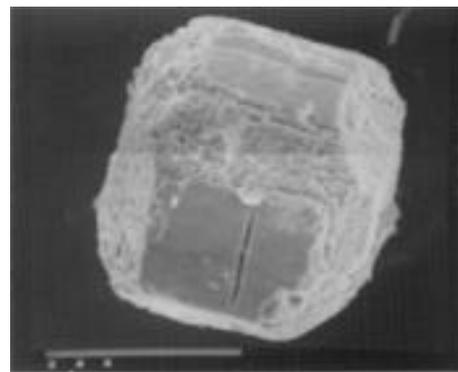
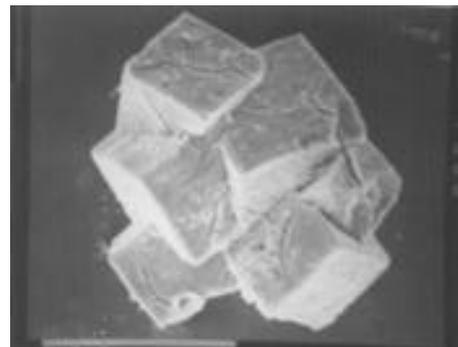
	Atomic percentage (at.%)						Weight percentage (wt%)					
	La	Nd	Pr	Sm	Ce	Cl	La	Nd	Pr	Sm	Ce	Cl
Experimental	8.17	5.11	4.09	1.50	0.25	80.9	20.3	13.2	10.3	4.06	0.64	51.4
Calculated	8.60	5.20	4.20	1.60	0.40	80.0	21.0	13.2	10.4	4.24	0.98	50.2

contain the ions of four rare earths including La, Nd, Pr and Sm with traces of Ce. Table 2 gives the atomic and weight per cent of the contents of the UR. The EDAX of figure 4 shows peaks corresponding to all the four major rare earths La, Nd, Pr and Sm in the grown crystals of

didymium molybdate. Table 3 gives the experimentally and theoretically calculated atomic and weight per cent of the rare earths present in the crystal. The agreement between the experimental quantitative estimation and theoretically calculated values suggest the molecular

Table 3. Data from EDAX analysis of $\text{Di}_2\text{Mo}_7\text{O}_{24}$.

	Atomic percentage (at.%)					Weight percentage (wt%)				
	La	Nd	Pr	Sm	Mo	La	Nd	Pr	Sm	Mo
Experimental	9.71	3.40	2.29	0.39	84.2	13.1	4.76	3.13	0.57	78.4
Calculated	13.6	4.78	3.22	0.55	77.8	17.9	6.51	4.29	0.79	70.5

**Figure 5.** Different morphologies of didymium molybdates.**Figure 7.** A crystal exhibiting layered growth.**Figure 6.** A regularly faceted crystal platelet with its plane faces.**Figure 8.** Twinned structure of didymium molybdates.

formula of the grown crystal to be $\text{La}_{1.23}\text{Nd}_{0.43}\text{Pr}_{0.29}\text{Sm}_{0.05}\text{Mo}_7\text{O}_{24}$. The EDAX did show some traces of Ce but the quantity is of negligible amount which was ignored. The proposed molecular formula of the crystals grown suggests it to be didymium heptamolybdate of the type $\text{R}_2\text{Mo}_7\text{O}_{24}$.

It is interesting to have a look at the morphology of mixed crystals obtained by the crystal growth method adopted here. The morphology of the crystals is described here.

Figure 5 shows different types of morphologies of didymium molybdates as viewed under scanning electron microscope. The various types of morphologies include spherulites, platelets, cuboids and coalesced crystals. It is interesting to see that most of the crystal surfaces are plane, devoid of any growth structures on them. Figure 6 shows regularly faceted crystal platelet with its plane

faces. A crystal exhibiting layered growth is shown in figure 7. One may notice that these crystals develop cracks produced due to vacuum coating or electron beam heating under the SEM which suggests the crystals are thermally unstable and may be carrying water of hydration. The details of their thermal behaviour as revealed by thermoanalytical studies conducted on them by TGA/DTA/DSC techniques are being worked out and will be published elsewhere. Sometimes twinned crystals are also obtained. Figure 8 is an example of twinned structures in didymium molybdates.

4. Conclusions

From the above described experiments and results, the following conclusions are drawn:

(I) Employing single gel single tube crystallizer, and using didymium chloride as the upper reactant and a solution prepared from $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\text{-NH}_4\text{NO}_3\text{-HNO}_3$ as the lower reactant impregnated in sodium meta silicate gel, leads to crystallization of didymium (a mixture of four rare earths La, Nd, Pr and Sm) heptamolybdate, bearing composition $\text{La}_{1.23}\text{Nd}_{0.43}\text{Pr}_{0.29}\text{Sm}_{0.05}\text{Mo}_7\text{O}_{24}$.

(II) The gel grown didymium heptamolybdate crystals assume varied morphologies including spherulites, cuboids, platelets, multifaceted and coalesced crystals. Twinned structures are also formed.

(III) The crystals grow mainly by two-dimensional spreading and piling up of layers, suggesting growth of crystals at high supersaturation.

References

- Bhat S, Kotru P N and Kaul M L 1995 *Mater. Sci. & Engg.* **B34** 138
- Belikova G S and Belyaev I M 1962 *Growth of crystals* (eds) A V Shubnikov and N N Sheftal (New York: Consultants Bureau) **3** p. 228
- Borchardt H J and Bierstedt P E 1966 *Appl. Phys. Lett.* **8** 50
- Dennis J and Henisch H K 1967 *J. Electrochem. Soc.* **114** 263
- Dharma Prakash S M and Rao Mohan 1987 *Cryst. Res. Technol.* **22** 1095
- Dishovsky N and Boncheva Z-MLadenova 1981 *J. Cryst. Growth* **51** 147
- Gits S, Robert M C and Lefauchese L 1985 *J. Cryst. Growth* **71** 203
- Jain A, Kotru P N and Kaul M L 1996 *J. Mater. Sci. Technol.* **12** 81
- Klevtsov P V, Kozeeva C P, Klevtsova R F and Novgorodtseva N A 1975 *Growth of crystals* (eds) N N Sheftal and E I Givargizov (New York: Consultants Bureau) **9** 107
- Kotru P N and Raina K K 1986 *J. Mater. Sci. Lett.* **5** 760
- Kotru P N, Razdan A K and Wanklyn B M 1989a *J. Mater. Sci.* **24** 2401
- Kotru P N, Razdan A K and Wanklyn B M 1989b *J. Mater. Sci.* **24** 793
- Pandita S, Hangloo V, Bamzai K K, Kotru P N and Sahni Neera 1998 *Semiconductor materials: Characterization and device applications* (ed.) R K Bedi (Amritsar: GND Univ.)
- Patel A R and Arora S K 1977a *J. Cryst. Growth* **37** 343
- Patel A R and Arora S K 1977b *Krist. Tech.* **13** 343
- Subba Rao U V and Babu Hari 1978 *Pramana-J. Phys.* **11** 147
- Subba Rao U V and Babu Hari 1980 *Indian J. Phys.* **A54** 147
- Wiktorowska B, Borecka B and Karniewicz J 1983 *J. Mater. Sci.* **18** 416