

## Growth and characterization of rare-earth mixed single crystals of samarium barium molybdate

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MS received 11 September 1991; revised 24 January 1992

**Abstract.** Molybdate crystals doped with rare-earth ions are finding immense use as laser materials. Rare-earth mixed single crystals of samarium barium molybdate grown in silica gel are important for use in optical equipment and electronic and acoustic studies. These octahedral bipyramidal crystals of samarium barium molybdates are characterized by IR, EDAX and thermal analyses.

**Keywords.** Rare earth crystals; samarium barium molybdate.

### 1. Introduction

The physical properties of the ferroelectric–ferroelastic rare-earth molybdates are of great interest in electro- and acousto-optical devices (Barkley *et al* 1971, 1972; Sapriel and Vacher 1977). Packter (1977) obtained BaMoO<sub>4</sub> as tetragonal bipyramidal crystals by the precipitation of alkaline-earth metal molybdate powders from neutral aqueous solution. We report here the growth of rare-earth mixed single crystals of samarium barium molybdate grown in silica gel. These crystals are identified and characterized by different methods.

### 2. Experimental

AnalaR grade sodium metasilicate was used for preparation of the gel. Silica gel (density 1.035 g cm<sup>-3</sup>) impregnated with standard solution (Ittyachen and Kurien 1979) of ammonium molybdate was used. The nitric acid content in the standard solution was used to adjust the pH of the gel. A mixed solution of samarium nitrate and Ba(NO<sub>3</sub>)<sub>2</sub> of different molarity was poured gently over the gel after complete gelation. As the outer electrolyte was added, it diffused into the gel to form light yellowish precipitate. This precipitate gradually increased in thickness and after it attained a certain thickness, dissolution started from the bottom of the precipitate. This led to nucleation growth of the crystals within the precipitate and just below it. The crystals acquired an average size of 2 × 1 × 1 mm within a month's time. Figure 1 shows a typical octahedral bipyramidal crystal of samarium barium molybdate.

For harvesting well-faceted good crystals the optimum condition was found to be 0.5 M of barium and samarium nitrates and a pH of 8 for the gel medium impregnated with IM standard solution (Ittyachen and Kurien 1979).

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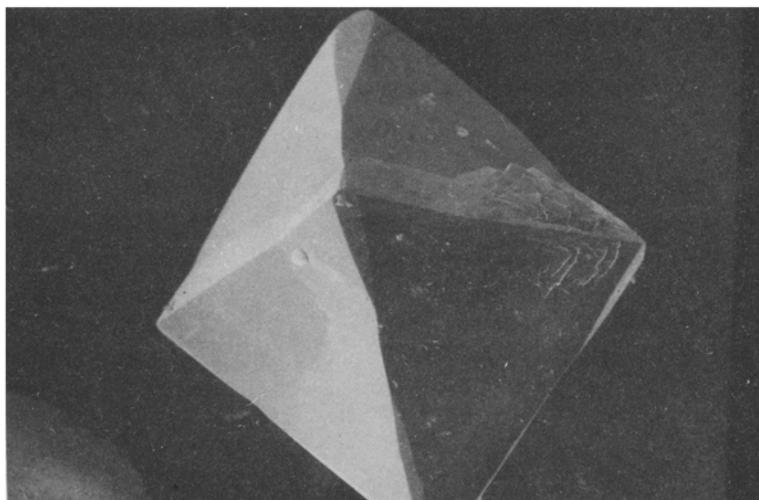


Figure 1. A typical octahedral bipyramidal crystal of samarium barium molybdate ( $\times 100$ ).

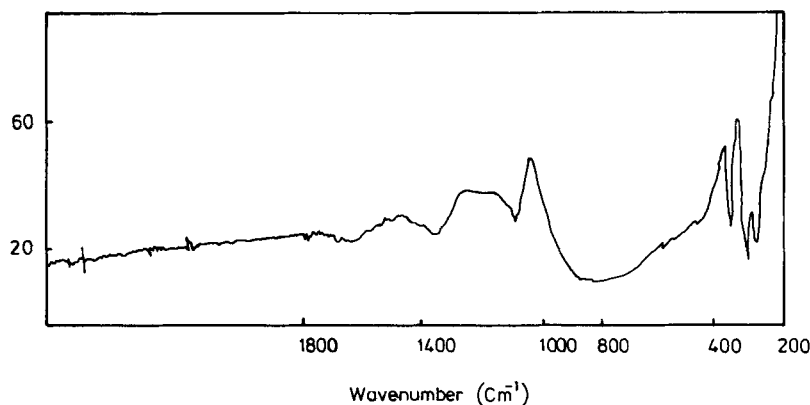


Figure 2. Infrared spectra of samarium barium molybdate.

### 3. Characterization

#### 3.1 Infrared analysis

The IR spectra of the samarium barium molybdate crystals (figure 2) were recorded employing the kBr pellet technique (Perkin Elmer spectrophotometer 983). The strong, broad intensive band peak observed at  $825\text{ cm}^{-1}$  was due to symmetric or antisymmetric stretching vibrations of the molybdate ion ( $\text{MoO}_4^{2-}$ ) (Busy and Keller 1964). The very weak line observed at  $1650\text{ cm}^{-1}$  was the first overtone of the line at  $825\text{ cm}^{-1}$ . The strong line at  $370\text{ cm}^{-1}$  was the antisymmetric bending vibration and the lines at  $325$  and  $290\text{ cm}^{-1}$  were due to the symmetric bending vibration of the molybdate ion (Clark and Doyle 1966).

The band at  $1350\text{ cm}^{-1}$  was indicative of the vibration of oxygen ion for pure samarium and barium. The IR band at  $800\text{--}850\text{ cm}^{-1}$  was assigned to M–O band

(Packter and Omono 1984) where  $M = \text{Sm} + \text{Ba}$ . The peaks at  $810(\gamma_3)$ ,  $325(\gamma_2)$  and  $370(\gamma_4)\text{cm}^{-1}$  were assigned to the characteristic absorption bands relating to  $(\text{MoO}_4)^{4-}$ . The peaks at  $600\text{cm}^{-1}(\text{w})$  and  $480\text{cm}^{-1}(\text{vw})$  were related to the Mo–O–Mo bands which agreed with Tsutomu *et al* (1980) and Nakamoto (1978).

### 3.2 TGA and DSC analyses

The thermogravimetric plot of the samarium barium molybdate was obtained using delta series TGA 7 at the scanning rate of  $20^\circ\text{C}/\text{min}$  (figure 3). This plot showed that the samarium barium molybdate crystals were found volatile at about  $400^\circ\text{C}$  temperature and the residue obtained at  $870^\circ\text{C}$  was only 1.988%.

Differential scanning calorimetric analysis was done using a delta series DSC 7 at the scanning rate of  $20^\circ\text{C}/\text{min}$ . No particular heat flow peak was obtained (figure 4).

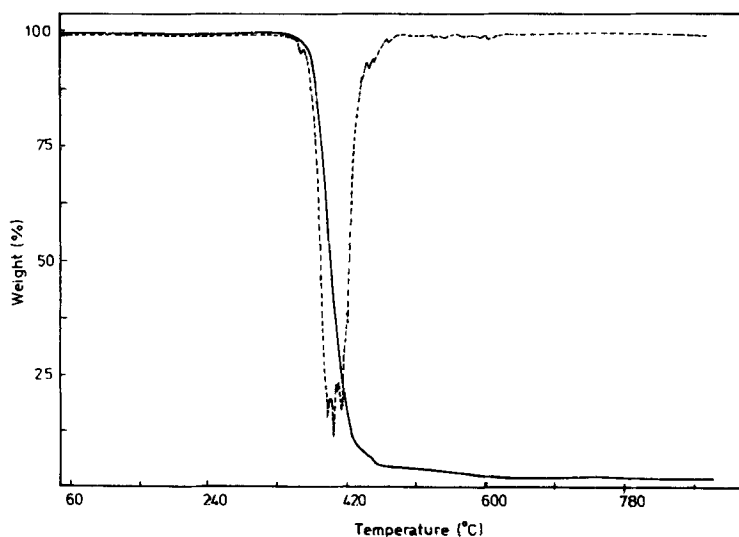


Figure 3. Thermogravimetric sketch of the crystal.

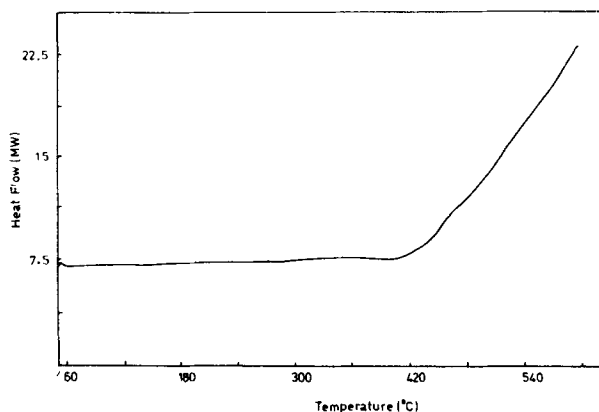


Figure 4. Differential scanning calorimetric sketch of  $\text{Sm}_2\text{Ba}_{1.53}\text{Mo}_{2.20}\text{O}_{8.16}$ .

## 3.3 EDAX

EDAX of the samarium barium molybdate crystals was carried out using EDAX recorder (no. 9226 IN model 1085) at the rate of 3393 CpS (FS 3657 CNT) in KV = 60 line with a tilt of  $2\theta$ . The results are given in table 1.

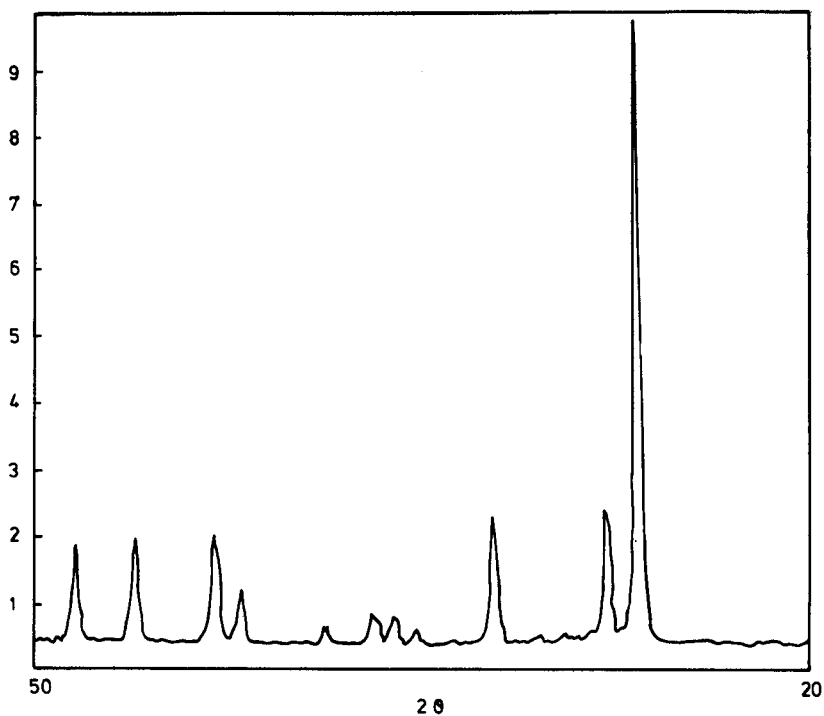
The oxygen radical in the crystal could not however, be detected by EDAX, since the constituent element was below the detectable limit of the instrument. From the data obtained the molecular formula of the crystal was determined as  $\text{Sm}_2\text{Ba}_{153}\text{Mo}_{220}\text{O}_{816}$ .

## 3.4 X-ray analysis

The X-ray diffraction pattern of the crystals was recorded using a Philips model pw 1710 with nickel filtered  $\text{CuK}_\alpha$  radiations (35 kV, 10 MA) of wavelength  $1.5418 \text{ \AA}$ . The characteristic diffraction pattern is shown in figure 5 and the  $d$  values in table 2.

**Table 1.** Results of EDAX.

Element	Cps	At element (%)
Bal	201-9071	49-60
SML	2-2481	0-71
MOK	103-4333	49-68
		100-00



**Figure 5.** X-ray diffraction pattern.

**Table 2.** X-ray powder data.

$2\theta$	$\theta$	$d(\text{nm})$	Intensity values ( $I$ )	$I/I_0$
26.6	13.3	3.3517	9.75	100
27.8	13.9	3.2094	2.4	24.62
32.2	16.1	2.7800	2.3	23.59
35.2	17.6	2.5501	0.6	6.15
36.1	18.05	2.4883	0.8	8.42
36.8	18.4	2.4426	0.85	8.95
38.7	19.35	2.3268	0.65	6.67
42.0	21.0	2.1515	1.2	12.63
43.0	21.5	2.1034	2.0	20.51
46.1	23.05	1.9690	1.95	20.00
48.4	24.2	1.8807	1.85	18.97

#### 4. Conclusion

Precipitation-cum-dissolution controlled mechanism of the growth of samarium barium molybdate crystals has no doubt emerged as a useful method of growing good crystals. The crystals are identified and characterized by different methods.

#### Acknowledgement

The authors wish to thank the authorities of IIT, Madras and the Physics Department, Banaras Hindu University, Varanasi for the help in analytical work. One of the authors (JI) is thankful to the Principal, C M S College, Kottayam for encouragement.

#### References

- Barkley J R, Brixner L H and Hogan E M 1971 *IEEE Symp. on the Application of ferroelectrics, York Town Heights, New York*
- Barkley J R, Brixner L H, Hogan E M and Waring R K 1972 *J. Ferroelectrics* **3** 191
- Busy R H and Keller O L Jr. 1964 *J. Chem. Phys.* **41** 215
- Clark Q M and Doyle W P 1966 *Spectrochim Acta* **22** 1441
- Ittyachen M A and Kurien K V 1979 *J. Cryst. Growth* **47** 743
- Nakamoto K 1978 *Infrared and Raman spectra of inorganic and coordinated compounds*. (New York: John Wiley) 3rd ed. p. 142
- Packter A 1977 *Krist. Tech.* **12** 729
- Packter A and Omono A 1984 *Crystal Res. Technol.* **19** 467
- Sapriel J and Vacher R 1977 *J. Appl. Phys.* **48** 1191
- Tsutomu M and Nasami T 1980 *J. Non Cryst. Solids* **38 & 39** 289