Chapter 5

OBSERVATIONS ON THE GROWTH
AND CHARACTERIZATION OF MIXED CRYSTALS OF
NEODYMIUM BARIUM MOLYBDATE
5.1. Introduction

Different from the normal way of crystal growth in gels, in which two nutrient solutions are allowed to interact in the gel medium, the growth of neodymium barium molybdate by two stage reaction is made use of in this chapter as in the 4th chapter. In the first stage, one of the reactants is incorporated in the gel as a colloidal solution and the other nutrient is allowed to diffuse into the gel to produce precipitate. The acid content in the gel creates dissolution and hence crystallization in the second stage.

This chapter deals with the growth of neodymium barium molybdate crystals in silica gel, the nucleation mechanism by which it grew, the influence of concentration of reagents and pH of the gel and the morphology of the crystals formed. These crystals were characterized by X-ray, IR, Laser Raman, UV-visible-near infrared, EDAX, ICP, XRF and thermal analyses.

5.2 Experimental

The crystallization apparatus used for the growth of crystals consists of a test tube 2.5 cm in diameter and 15 cm in length. A quantity of 20ml of sodium metasilicate
solution (analytical grade) of specific gravity 1.03 whose pH was adjusted by titration with '1S' standard solution (as in chapter 4) of ammonium molybdate, was allowed to gel in a test tube at room temperature. After the perfect setting of the gel a mixed solution of neodymium nitrate and barium nitrate of different molar ratio was gently poured drop by drop over the gel without breaking the gel surface. When the outer electrolyte was added over the gel, the ions diffused into the gel to form suitable conditions for crystallization.

5.3 Growth procedure

First electrolyte was impregnated with the gel and the acidity of the '1S' standard solution determined the pH of the gel. Experiments were done with the gel having a pH between 4 and 8. When the second electrolyte was poured over the gel, a layer of light violetish precipitate was formed. The thickness of the precipitate increased with time. After the precipitate reached a considerable thickness, dissolution started from the bottom region towards the gel solution interface up to a certain distance depending upon the concentration of the nutrients and the pH of the gel. The experimental set up is shown in figure (5.1). Dissolution led to crystallization and the crystals so formed within 25-30 days were of an average
size of 0.3mm x 0.2mm x 0.1mm. These crystals were observed using optical and scanning electron microscopes. Fig (5.2) shows a set of typical crystals in low magnification.

Details of the experimental conditions for the growth of the neodymium barium molybdate crystals are shown in table (5.1).

5.3.1 Effect due to change in concentration of the nutrients

According to the change in the concentration of the inner and outer electrolyte, there was change in the depth of the precipitate, dissolution and region of crystallization. The time-displacement curve of precipitation and dissolution fronts according to the change in the outer electrolyte is shown in fig. 5.3 (pH = 8) and fig 5.4 (pH = 7).

As the concentration of the outer electrolyte increased, the thickness of the precipitate also increased. The partial dissolution started from the bottom region of the precipitate towards the gel-solution interface which was proportional to the concentration of the outer electrolyte. At the same time, it was reversely
Table 5.1

Experimental Conditions for the Growth of Neodymium Barium Molybdate Crystals in Gel

| Density of gel solution | = 1.03gcm⁻³
| Temperature of growth | = 28°C
| Age of gel | = one day
| Growth period | = 25-30 days
| Growth apparatus | = a single tube of size 2.5cmx15cm.
| Inner electrolyte | = 1M standard solution of ammonium molybdate
| Outer Electrolyte | = neodymium nitrate + barium nitrate.

<table>
<thead>
<tr>
<th>pH Value</th>
<th>Outer Electrolyte</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>0.5 M</td>
<td>light violetish ppt. + almost dissolution, numerous crystals of clustered, twinned and singlets.</td>
</tr>
<tr>
<td></td>
<td>0.1 M</td>
<td>ppt. + dissolution crystal-dendritic, + singlets</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>no ppt.</td>
</tr>
<tr>
<td>7</td>
<td>0.5 M</td>
<td>more thick ringular ppt. crystals - density decreased, majority twinned, no so perfect</td>
</tr>
<tr>
<td></td>
<td>0.1 M</td>
<td>ppt.+dissoln. crystals-large clustered, small singlets</td>
</tr>
<tr>
<td></td>
<td>0.01 M</td>
<td>no ppt., but nucleation</td>
</tr>
<tr>
<td>6</td>
<td>0.5 M</td>
<td>ppt. - clearly separated disc pattern at bottom, crystals-no singlets, clustered (0.19cmx0.21cm) and spherulites.</td>
</tr>
<tr>
<td></td>
<td>0.1 M</td>
<td>few clustered crystals</td>
</tr>
<tr>
<td></td>
<td>0.01 M</td>
<td>no ppt.</td>
</tr>
<tr>
<td>5</td>
<td>0.5 M</td>
<td>thick discular ppt. thickness of discs decreases downwards</td>
</tr>
<tr>
<td></td>
<td>0.1 M</td>
<td>no crystal.</td>
</tr>
<tr>
<td></td>
<td>0.01 M</td>
<td>traditionally no crystal,discular ppt.</td>
</tr>
<tr>
<td>4</td>
<td>0.5 M</td>
<td>equally spaced (upto 10) discular ppt., dissoln.</td>
</tr>
<tr>
<td></td>
<td>0.1 M</td>
<td>no crystal.</td>
</tr>
<tr>
<td></td>
<td>0.01 M</td>
<td>ringular ppt. no crystal.</td>
</tr>
</tbody>
</table>

ppt. = precipitate, dissoln. = dissolution

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Fig. 5.3 Rate of displacements of precipitation and dissolution fronts due to the change in the outer electrolyte (pH = 8).

Fig. 5.4 Rate of displacements of precipitation and dissolution fronts due to the change in the outer electrolyte (pH = 7).
affected by the increase in the inner electrolyte. The dissolution was forced by the acid content in the inner electrolyte and this led to the crystallization of light violetish white transparent neodymium barium molybdate mixed crystals.

The average growth rates of crystals of bipyramidal orthorhombic habits nucleated towards the bottom of the test tube were calculated. Fig (5.5) shows the plot of square of the length of the crystal versus time of growth in gel for various outer solution concentrations.

5.3.2 Effect due to change in pH of the gel

The pH of the gel was found to be a critical parameter in the formation of precipitate, dissolution and growth of crystals. The effect of pH on the precipitation and partial dissolution front movement are shown in figure (5.6). The thickness of the precipitate increased with the decrease in pH values of the gel. Crystallization was found to be possible in the gel at a pH between 6 and 8. Below these pH values no crystallization was obtained.

The optimum condition for harvesting well faceted good crystals was found to be in a pH of 8 of the gel, which was impregnated with '1S' standard solution, with a
Fig. 5.5 Square of length versus time of growth of gel grown bipyramidal octahedral crystals for different outer electrolyte concentration.

Fig. 5.6 Plot showing time-displacement of precipitation and partial dissolution fronts due to change in pH of the gel.
mixture of 0.05M barium nitrate and neodymium nitrate used as the outer electrolyte. Instead of barium nitrate, barium chloride can be used to obtain the same crystals.

5.3.3 Morphology of the crystals

The best conditions for the growth of good quality crystals were at a pH between 6 and 8 of the gel. At pH 6 of the gel, the precipitate was arranged in Liesegang rings, along with fine single crystals. At and below a pH 5 of the gel only Liesegang rings were observed.

Crystals of various morphologies were observed. The majority of them were bipyramidal octahedral in shape. SEM photographs of these type of crystals are shown in figure (5.7). Some of the crystals were found to be twinned at the middle part as in figs. (5.8) & (5.9). The boundary of twinning is clearly visible in the photograph. Figure (5.10) shows a typical octahedral crystal with growth layers on its octahedral faces. The growth layers were found to be thick and had the morphology of the face. The mechanism of the growth may be due to the two-dimensional nucleation and spreading mechanism. The majority of the crystals were found to be having faces with no growth layers. The growth layers found on some crystals may be due to local variation of concentration.
gradient in the system. Figure (5.11) shows a typical case of multiple crystals radiating out of a common centre. These types of crystals were mainly observed, together with spherulites in the region very near to the interface at higher pH values. Multiple crystals were formed as a result of diffusion of highly concentrated nutrients near the interface. It can be observed that the faces of the individual crystals protruding from the centre were all curved. This is also an evidence of the nature of the higher concentration of the nutrients.

At a pH of 7 of the gel, no perfect single crystals were obtained. Twinned, clustered patterns were found. At a pH 6 of the gel, very few clustered and twinned crystals along with independent spherulites and clear discular Liesegang rings were observed (Fig. 5.12).

5.4. Characterization

5.4.1 XRD analysis

X-ray spectroscopy provides much useful information about the structure of crystals.

In order to confirm the crystallinity of neodymium barium molybdate, the powder X-ray diffraction pattern of the crystal was taken with a Philips XRD model PW 1050/70
FIGURE CAPTIONS

Fig. 5.1 Experimental set up of the mixed crystals neodymium barium molybdate grown in silica gel.

Fig. 5.2 A typical set of crystal at lower magnification x 50.

Fig. 5.7 SEM photograph of the crystal of different morphology x 100.

Fig. 5.8 A magnified photograph of one of the crystals of fig.(5.7), which is twinned x 260.

Fig. 5.9 SEM photograph of a typical twinned crystal x 240.

Fig. 5.10 A typical octahedral crystal with additional growth layers on its (011) and (101) faces. x 440

Fig. 5.11 A typical multiple crystal radiating out of a common centre x 320.

Fig. 5.12 Formation of crystals, spherulites and Liesegang rings at particular condition (pH = 6).
with nickel filtered CuKα radiations (\(\lambda = 1.5418\) Å) as in fig. (5.13). The 'd' values computed for the assigned hkl values are given in table (5.2).

It was found that neodymium barium molybdate is crystalline, belonging to the orthorhombic system with lattice parameters \(a = 7.734(3), b = 7.961(3)\) and \(c = 11.405(6)\) Å respectively.

5.4.2 IR analysis

The infrared spectrum of the crystal was recorded by employing PE 580 spectrophotometer in KBr matrix (Fig. 5.14). The intense band observed at \(810\) cm\(^{-1}\) is the merged peak due to symmetric and antisymmetric stretching vibrations of the molybdate ion \((\text{Mo}O_4)^{2-}\) [222]. The medium intensity line observed at \(1620\) cm\(^{-1}\) is due to the first overtone of the line at \(810\) cm\(^{-1}\). The band observed in the region \(800-850\) cm\(^{-1}\) has been assigned to M-O band[223]. Where \(M = \text{Nd+Ba}\). The peaks at \(810\) cm\(^{-1}\) \((\nu_1 + \nu_3)\), \(373\) cm\(^{-1}\) \((\nu_4)\) and \(330\) cm\(^{-1}\) \((\nu_2)\) relating to \((\text{Mo}O_4)^{4-}\) agree quite satisfactorily with the literature of Nakamoto[224] and Clark[225]. The weak peaks at \(460\) cm\(^{-1}\) and \(660\) cm\(^{-1}\) correspond quite well with the \(\nu_{\text{sym.}}\) and \(\nu_{\text{antisym.}}\) modes of Mo-O-Mo oxygen bridge band[226].
Fig. 5.13 XRD pattern of neodymium barium molybdate mixed crystal.
Table 5.2

X-RAY POWDER DATA

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>hkl</th>
<th>2 Theta</th>
<th>I/I\text{max.}</th>
<th>d (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>200</td>
<td>26.7867</td>
<td>17</td>
<td>3.8651</td>
</tr>
<tr>
<td>2</td>
<td>211</td>
<td>31.2333</td>
<td>52</td>
<td>3.3258</td>
</tr>
<tr>
<td>3</td>
<td>202</td>
<td>32.4600</td>
<td>77</td>
<td>3.2033</td>
</tr>
<tr>
<td>4</td>
<td>220</td>
<td>37.6733</td>
<td>53</td>
<td>2.7729</td>
</tr>
<tr>
<td>5</td>
<td>133</td>
<td>50.5533</td>
<td>100</td>
<td>2.0967</td>
</tr>
<tr>
<td>6</td>
<td>205</td>
<td>54.2333</td>
<td>23</td>
<td>1.9642</td>
</tr>
<tr>
<td>7</td>
<td>402</td>
<td>58.5267</td>
<td>27</td>
<td>1.8315</td>
</tr>
<tr>
<td>8</td>
<td>242</td>
<td>63.8933</td>
<td>36</td>
<td>1.6920</td>
</tr>
<tr>
<td>9</td>
<td>037</td>
<td>054</td>
<td>440</td>
<td>1.3885</td>
</tr>
</tbody>
</table>

Orthorhombic system

unit cell dimensions : $a = 7.734$ (3)  
                      $b = 7.961$ (3)  
                      $c = 11.405$ (6)
Fig. 5.14. Infrared spectrum of neodymium barium molybdate mixed crystal.
5.4.3 Laser Raman spectra analysis

Laser Raman spectrogram, fig. (5.15) & (5.16), was recorded using the Cary model -82 Laser Raman spectrometer which makes use of an Ar$^+$ & Kr$^+$ laser. In the stretching region (750-950 cm$^{-1}$) there were peaks at 885, 835 and 785 cm$^{-1}$ and in the bending region the peaks obtained were at 360, 340 and 325cm$^{-1}$. The frequency at 190cm$^{-1}$ is related to rotational and at 135, 110, 75 and 50cm$^{-1}$ are related to translational frequencies. Weak peaks 2190, 2110, 2070 and 1800cm$^{-1}$ were also observed in the medium region.

5.4.4 UV-visible - near infrared analysis

The spectrogram is shown in fig. (5.17). The peak obtained at 575.5 nm indicate the presence of neodymium in the crystal[227,228] and the peaks at 307.1 &413 nm give evidence of the presence of barium[229] in the crystal.

5.4.5 Energy dispersive X-ray analysis (EDAX)

The EDAX plot was recorded using EDAX No.711 as shown in fig. (5.18). The three dominant peaks at 4.46, 4.82 and 5.156 Kev correspond quite well with the L$\alpha$, L$\beta$, L$\gamma$, energies of barium while lesser intense peaks at 5.23, 5.72, 6.088 Kev correspond to L$\alpha$, L$\beta$, L$\gamma$. 

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Prepared by BeeHive Digital Concepts Cochin for Mahatma Gandhi University Kottayam
Fig. 5.15. Raman spectrum of neodymium barium molybdate mixed crystal (Range: 30-1300 cm\(^{-1}\))
Fig. 5.16. Raman spectrum of neodymium barium molybdate mixed crystal (Range: 1400-2600 cm\(^{-1}\))
Fig. 5.17. uv-visible-near infrared absorption spectrum of neodymium barium molybdate crystal. (Range: 300-450 and 500-650).
energies of neodymium giving a clue that barium is dominant over neodymium in the crystal. The well defined large peak at 2.26 Kev relates to the molybdenum present in the form of molybdate in the crystal. From this, the presence of barium, neodymium and molybdenum assigned from the EDAX peaks was quite well in agreement with the EDAX international chart. The integrated counts of X-ray photoelectrons relating to barium (Lα) collected for 150 seconds were found to be 20,349 while for neodymium (Lα) the counts were 6,400.

From the integrated counts obtained it can be calculated that the percentage of Nd = 23.927 and Ba = 76.073 ie., Nd and Ba are incorporated in the crystal in the ratio 3:10. The formula can be given as Nd₆Ba₂₀(Mo₄)₂₉⁻ or [Nd₆Ba₂₀Mo₂₉O₁₁₆]

5.4.6 XRF analysis

X-ray crystal used for the XRF analysis was LiF 220°. The peaks were obtained at 112.68° (Lα), 128.79° (Lα) and 28.90° (Kα) respectively (Fig 5.19). These are characteristic of the elements in the crystal which confirm the presence of neodymium, barium and molybdenum respectively.
Fig. 5.18. EDAX pattern of neodymium barium molybdate mixed crystal.
Fig. 5.19. XRF spectrum of the neodymium barium molybdate mixed crystal.
5.4.7 Thermal analyses

A thermogravimetric plot (fig. 5.20) of neodymium barium molybdate was taken using a TGA Dupont 2000 in \( N_2 \) (10 LAR) 50 ML/MIN. This plot showed that the neodymium barium molybdate crystal is volatile at about a temperature of 400\(^\circ\)C and very little residue is obtained at 500\(^\circ\)C.

Differential thermal analysis was done using DTA Dupont 2000. The DTA plot of the crystal is shown in fig. (5.21). No particular peak or transition was observed before decomposition.

5.5 Conclusion

Gel growth is found to be the best technique for growing rare earth mixed crystals like neodymium barium molybdate. The various habits found at different regions in the gel are believed to have been formed due to the blocking of the counter diffusion of the two reacting top solutions[230]. The pH of the gel, concentration of the inner and outer electrolytes play an important role in crystallization. The crystals are identified and characterized by different methods.
Fig. 5.20. TGA plot of neodymium barium molybdate mixed crystal.
Fig. 5.21. DTA plot of neodymium barium molybdate mixed crystal