CHAPTER 5

SINGLE CRYSTAL GROWTH OF LANTHANUM MOLYBDATE (La₄Mo₇O₂₇) USING H₃BO₃ FLUX

5.1 INTRODUCTION

In the past few decades, due to the fast development of the laser technique, nonlinear optical (NLO) crystals have been playing an important role and have been widely used in high-speed information processing, optical data storage, laser medicine, laser frequency conversion, signal communications, optical modulating, etc. in the expanding field of integrated optics (Dmitriev et al 1999, Burland et al 1994, Chen and Liu 1986, Sasaki et al 2000). Rare-earth elements have unique characteristics unlike most other elements on the periodic table. These consist of thirty elements all together separated into two different groups, lanthanides (fifteen total) and actinides (fifteen total). The lanthanides are elements famous for their 4f shell level that resides deep inside the atom itself. Each lanthanide contains a 4f orbital shielded by 4d and 5p orbital electrons. Electrical, optical, photonic and thermal uses were deduced from research with each rare-earth element. The extensive research for the new rare earth (R) and other element complex borates are of great interest because of their potential applications in nonlinear optics (NLO) and laser engineering. The isoformular compounds Eu₄Mo₇O₂₇ (Naruke and Yamase 2001) and Gd₄Mo₇O₂₇ (Naruke and Yamase 2002) have a similar structure.

The flux growth technique is particularly preferable because it readily allows crystal growth at a temperature well below the melting point of
the solute. In addition, crystals grown from flux have an enehedral habit and a reasonably lower degree of dislocation density. In this chapter, the flux growth of $\text{La}_4\text{Mo}_7\text{O}_{27}$ single crystals by a high temperature solution growth technique or flux growth method using $\text{La}_2\text{O}_3$, $\text{MoO}_3$ and $\text{H}_3\text{BO}_3$ used as a flux and investigation of some useful physical properties of the crystals are presented. The structure of the $\text{La}_4\text{Mo}_7\text{O}_{27}$ crystal was first described by Benjamin van der Wolf et al (2009). $\text{La}_4\text{Mo}_7\text{O}_{27}$ crystallizes in the orthorhombic system, space group $\text{Pca2}_1$, with $a = 14.1443$ (14) Å, $b = 7.2931$ (4) Å, $c = 22.9916$ (13) Å, $V = 2371.7$ (3) Å$^3$ and $Z = 4$. For the growth of crystals by flux method, not only the nature of flux is important, but also the ratio of flux is essential. Many trials were made to obtain a good transparent crystal from flux growth. Nevertheless, these materials also have some intrinsic weaknesses, and it is typically difficult to grow high-quality crystals to a size for optical applications.

5.2 SYNTHESIS AND CRYSTAL GROWTH

Crystals of the orthorhombic phase $\text{La}_4\text{Mo}_7\text{O}_{27}$ (lanthanum molybdenum oxide) were obtained from a non-stoichiometric melt in the pseudo-ternary system $\text{La}_2\text{O}_3$–$\text{MoO}_3$–$\text{B}_2\text{O}_3$. The title compound of $\text{La}_4\text{Mo}_7\text{O}_{27}$ was synthesized using high-temperature solid-state technique. The initial substances were $\text{La}_2\text{O}_3$ (99.99%, AlfaAesar), $\text{H}_3\text{BO}_3$ (99.8%, Merck) and $\text{MoO}_3$ (99.95%, Himedia) in a molar ratio of 0.16: 0.16: 0.68. An excess of $0.5 – 0.8$ mol $\text{H}_3\text{BO}_3$ was added to compensate any loss due to vaporization of $\text{H}_3\text{BO}_3$ in the process of high-temperature reaction. The experiments were carried out in a resistance-heated furnace. A controller (Eurotherm, model No. 2704) with an accuracy of $\pm 0.01^\circ\text{C}$ was used to control the furnace temperature. Figure 5.1 shows the schematic setup used for the growth of lanthanum molybdenum oxide single crystals. The furnace was made up of
silicon carbide rods and thick ceramic slabs are used as the walls of the furnace.

Figure 5.1 Schematic of furnace setup for the growth of La₄Mo₇O₂₇ single crystal by flux growth technique

The starting materials of: La₂O₃ (99.99%, AlfaAesar), H₃BO₃ (99.8%, Merck) and MoO₃ (99.95%, Himedia) were mixed in a molar ratio of 0.16: 0.16: 0.68 in a platinum crucible and preheated at 1023 K for 90 h to decompose the boron acid. After 95 h at this temperature the sample was quenched in air, washed with water at 60°C. A series of grinding and heating were performed prior to final heating at 827°C and cooled at a rate of 0.5 °C/h to 820°C and quenched again in air. Figure 5.2 shows the temperature profile of the experiment. A further similar heating-cooling cycle, colourless crystals of La₄Mo₇O₂₇ were obtained and separated mechanically from the solidified melt. The La₄Mo₇O₂₇ crystal was also very stable in air and in moist environments, which demonstrated that it is chemically stable and not hygroscopic. All samples obtained were checked by X-ray powder diffraction analysis to confirm the single-phase of La₄Mo₇O₂₇.
Figure 5.2 Temperature profile used for the growth of lanthanum molybdenum oxide single crystals

Several ratios of La$_2$O$_3$: H$_3$BO$_3$ : MoO$_3$ were tried for growing La$_4$Mo$_7$O$_{27}$ crystals, but the ratio 0.16: 0.16: 0.68, yielded crystals. Table 5.1 shows the experimental summary of the La$_4$Mo$_7$O$_{27}$ crystal growth. The present experimental investigation showed that La$_4$Mo$_7$O$_{27}$ crystals with good optical quality grown from H$_3$BO$_3$ solvent (flux). Transparent, colorless single crystals with dimensions (0.8×0.3×0.2 mm$^3$) were obtained. Figure 5.3 shows the as grown La$_4$Mo$_7$O$_{27}$ crystal from flux growth technique.
Table 5.1 Summary of the crystal growth Experiment

<table>
<thead>
<tr>
<th>La$_2$O$_3$:MoO$_3$:H$_3$BO$_3$</th>
<th>Temperature for crystallization ($^\circ$C)</th>
<th>Cooling rate ($^\circ$C/h)</th>
<th>Size and quality of crystals grown</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.16: 0.16: 0.68</td>
<td>827</td>
<td>1</td>
<td>Poor</td>
</tr>
<tr>
<td>0.16: 0.16: 0.68</td>
<td>827</td>
<td>0.5</td>
<td>(0.8×0.3×0.2 mm$^3$)</td>
</tr>
<tr>
<td>0.16: 0.16: 0.68</td>
<td>827</td>
<td>0.5</td>
<td>(0.2×0.2×0.1 mm$^3$)</td>
</tr>
<tr>
<td>0.16: 0.16: 1</td>
<td>827</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>0.16: 0.2: 2</td>
<td>827</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>0.16: 0.2: 3</td>
<td>827</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>0.16: 0.16: 0.68</td>
<td>827</td>
<td>1</td>
<td>Poor</td>
</tr>
</tbody>
</table>

Figure 5.3 As grown La$_4$Mo$_7$O$_{27}$ crystal from flux growth technique
5.3 RESULTS AND DISCUSSION

5.3.1 XRD Analysis

Powder XRD analysis of the $\text{La}_4\text{Mo}_7\text{O}_{27}$ was performed on the desktop Bruker, D2 Phaser Instrument with a diffracted-beamed monochromator set for CuKα ($\lambda = 1.5418\text{Å}$) radiation at room temperature in the angular range of $2\theta = 10$-70°, with a scan step width of 0.01°, and a fixed counting time of 1 s/step. The obtained powder XRD pattern is shown in Figure 5.4. The experimental PXRD pattern of $\text{La}_4\text{Mo}_7\text{O}_{27}$ is in good agreement with the literature data.

![Figure 5.4 Powder XRD pattern of $\text{La}_4\text{Mo}_7\text{O}_{27}$](image)

5.3.2 EDX Studies

The EDX analysis is a powerful tool in determining the presence of the constituent elements in a given sample. The EDX measurements were made using an INCA 200 energy dispersive X-ray micro-analyzer.
Figure 5.5 (a) shows surface region of sample for EDX analysis. The red colour square region indicates the experimental portion for EDX. The EDX spectrum is shown in Figure 5.5 (b) and the elemental composition is figured in Table 5.2. The presence of the constituent elements (Lanthanum, molybdenum and oxygen) of the $\text{La}_4\text{Mo}_7\text{O}_{27}$ crystal was confirmed by the occurrence of their respective peaks. There are no signs for the presence of flux in the crystal. Hence, the formation of ‘flux-free’ $\text{La}_4\text{Mo}_7\text{O}_{27}$ crystal is confirmed.

![Figure 5.5 (a) Surface region of the $\text{La}_4\text{Mo}_7\text{O}_{27}$ crystal, (b) the EDX spectrum of the $\text{La}_4\text{Mo}_7\text{O}_{27}$ crystal](image)

Table 5.2 Elemental composition of the $\text{La}_4\text{Mo}_7\text{O}_{27}$ crystal

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt%</th>
<th>At%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ok</td>
<td>27.97</td>
<td>70.92</td>
</tr>
<tr>
<td>MoL</td>
<td>61.49</td>
<td>26.00</td>
</tr>
<tr>
<td>LaL</td>
<td>10.54</td>
<td>03.08</td>
</tr>
</tbody>
</table>
5.3.3 SEM Studies

The SEM image (Figure 5.6) shows that the as grown lanthanum molybdenum oxide crystal exhibits uniform hexagonal shape. Most of the crystals were found to have hexagonal plate shape with typical edge angles of 45° and with very flat surfaces. The size of the one crystallite is about 3.85 µm length, 472.0 nm in diameter. The smooth surfaces and the sharp edges confirmed that these small single crystals were of high quality. Generally speaking, the growth morphology of a crystal is determined by the relative growth rates of all the possible faces.

![SEM micrographs of lanthanum molybdenum oxide crystals](image)

**Figure 5.6 SEM micrographs of lanthanum molybdenum oxide crystals**

5.3.4 UV-Vis Studies

The absorption spectrum of lanthanum molybdenum oxide is shown in Figure 5.7 (a). According to the experimental measurements, the crystal has a transparent region in the 455-2000 nm optical range with a cut off at 455 nm. The absorption decreases rapidly around 450 nm and leads to the efficient absorption. Therefore, there is little optical absorption in the
visible region of the UV–Vis–NIR spectrum. Crystals of lanthanum molybdenum oxide may be useful for applications in the wavelength region of 450-2500 nm. At the wavelength, just above 500 nm, there is a sudden increase in absorbance in the crystal due to electronic excitation of lanthanum molybdenum oxide. Since the crystal is possessing delocalized electron cloud for charge transfer, the absorbance is less between 500 and 2000 nm. Hence, the crystal can be used for SHG and optical applications (Bhat 1994).

![Absorbance spectrum of the grown lanthanum molybdenum oxide](image)

**Figure 5.7 (a) Absorbance spectrum of the grown lanthanum molybdenum oxide**

### 5.3.4.1 Optical band gap

Optical band gap of the material was calculated from the transmittance spectrum. The measured transmittance (T) was used to calculate the absorption coefficient (α) using the equations 2.1 and 2.2 given in the chapter 2. The band gap was calculated from the plot between hν and (αhν) \(^{1/2}\) as shown in the Figure 5.7 (b). The optical band gap is found to be 2.6 eV for lanthanum molybdenum oxide.
Photoluminescence (PL) Analysis

Photoluminescence is the process by which a material is bombarded with photons, becomes excited, and then emits photons back into the system from the given material. In this research, rare-earth elements are being excited by photons from a laser and their de-excitation is recorded from the photomultiplier tube inside the spectrometer. The optical behaviour of the title compound was analyzed by PL measurements. The photoluminescence spectrum was recorded for La$_4$Mo$_7$O$_{27}$ using HORIBA JOBINYVON Luminescence spectrometer. Argon ion laser ($\lambda = 488$ nm) was used as an input source and 2 mm slide width was used for studies. The excitation wavelength used for the present study is 488 nm. The recorded spectrum is shown in Figure 5.8, in which, the maximum intensity is observed around 534 nm. Generally, a green–yellow emission is observed in PL spectra, due to
recombination of photo generated holes with singly ionized charge state of specific defect (Hsieh et al 2003). However, absence of the green yellow emission in the sample indicates the potential of strategy to produce a low concentration of oxygen defects and high optical quality of single crystal La$_4$Mo$_7$O$_{27}$ (Zu et al 1997, Gao et al 2005). The emission of 534 nm could not contribute to the transition from the conduction band to the valence band. The emission does not originate from a transition between the conduction and valence band; it comes from a deep-level or trap-state emission.

![Photoluminescence spectrum of La$_4$Mo$_7$O$_{27}$ excited by a 488 nm laser](image)

**Figure 5.8** Photoluminescence spectrum of La$_4$Mo$_7$O$_{27}$ excited by a 488 nm laser

5.3.6 Thermal Analysis

The thermal stability of the material is a very important factor for potential application. In order to know the thermal stability of the material,
thermogravimetric analysis (TGA) as well as differential thermal analysis (DTA) were carried out on polycrystalline samples of La₄Mo₇O₂₇ in flowing N₂ ambient. For this purpose, a NETZSCH STA 409 C/CD simultaneous DT/TG analyser with a heating rate of 2.5 K/min was employed. The TGA thermogram is shown in Figure 5.9. From the figure, there is no weight loss between 30 and 100°C, hence there is no adsorbed water in the material between 100 and 400°C a gradual decrease in weight loss is noted is due to volatilization of boric acid. It was followed by a major weight loss at 800°C due to decomposition of La₄Mo₇O₂₇. Hence the compound stable up to 800°C.

![Figure 5.9 TG/DTG curves of La₄Mo₇O₂₇](image)

**Figure 5.9 TG/DTG curves of La₄Mo₇O₂₇**

### 5.3.7 Dielectric Studies

The dielectric study of La₄Mo₇O₂₇ was carried out using the instrument, HIOKI 3532-50 LCR HITESTER. The capacitance (C) and
quality factor (Q) of the sample at different temperatures and at a frequency were measured. The compounds were prepared in pellet form of circular cross section (area \( \sim 0.90 \times 10^{-4} \text{m}^2 \) and thickness \( \sim 0.30 \times 10^{-2} \text{m} \)) by applying pressure. The pellets were then sintered in air for 12 h at 50°C. The pellet covered with film of silver paint on the opposite surfaces to obtain a good contact was inserted between the two silver electrodes. The dielectric constant (\( \varepsilon' \)) of the sample was calculated using the equation 2.5 (given in the second chapter) and dielectric loss (\( \varepsilon'' \)) of the sample was calculated using the following equation (Cusac 1967, Suchet 1975)

\[
\varepsilon'' = \frac{\varepsilon'}{Q}
\] (5.1)

where Q is the quality factor respectively.

The plots of dielectric constant (\( \varepsilon' \)) and dielectric loss with frequency for various temperatures are shown in Figures 5.10 (a) and (b). The dielectric constant is high in the lower frequency region and variation of dielectric constant (\( \varepsilon' \)) with log f decreases with an increase in frequency. The very high value of dielectric constant at low frequencies may be due to the presence of all the four components namely, space charge, orientational, electronic and ionic polarisations. The dielectric loss was also studied as a function of frequency for different temperatures and is shown in Figure 5.10 (b). The low dielectric loss at high frequencies for the given sample indicates very high purity of the material. This parameter is of vital importance for nonlinear optical materials in their applications. These curves suggest that the dielectric loss is strongly dependent on the frequency of the applied field.
Figure 5.10 (a) Variation of dielectric constant ($\varepsilon'$) with log f

Figure 5.10 (b) Variation of dielectric loss ($\varepsilon''$) with log f
5.3.8 Second Harmonic Generation

A high-intensity Nd:YAG laser (\(\lambda = 1064 \text{ nm}\)) with a pulse duration of 10 ns was passed through the powdered sample of \(\text{La}_4\text{Mo}_7\text{O}_{27}\). The SHG behaviour was confirmed by the Kurtz - Perry powder technique (Kurtz and Perry 1968) from the output of the laser beam having the bright green emission (\(\lambda = 532 \text{ nm}\)). The second harmonic signal of 1.3 mV for \(\text{La}_4\text{Mo}_7\text{O}_{27}\) was obtained for an input energy of 2 mJ/pulse. But the standard KDP crystal gave a SHG signal of only 14.5 mV for the same input energy.

5.4 CONCLUSION

The single crystal of dimensions up to \(0.8 \times 0.3 \times 0.2 \text{ mm}^3\) \(\text{La}_4\text{Mo}_7\text{O}_{27}\) was grown by high-temperature solution growth technique (Flux growth) using \(\text{H}_3\text{BO}_3\) as flux and confirmed by X-ray diffraction and FTIR studies. The optical absorbance data gave maximum absorption from 500-2000 nm. Its optical band gap values and the refractive index (n) were calculated. The PL studies showed a sharp peak at 2.32 eV.