Growth and characterization of NLO crystal

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Pure ammonium dihydrogen orthophosphate (ADP) crystals and ADP crystals doped with nitrite tri-acetic acid and ethylene diamine tetra acetic acid (EDTA) have been grown by slow evaporation technique. Grown crystals have been characterized using X-ray diffraction and energy dispersive X-ray spectroscopy (EDAX). Second harmonic generation (SHG) efficiency measurements are carried out by Kurtz method. It has been found that the ADP crystals containing nitrite tri acetic acid and EDTA have resulted appreciable increase in SHG efficiency as compared to pure ADP crystals. Dielectric constant and dielectric loss are measured as a function of frequency. Study confirms the contribution of space charge polarization.

Keywords: ADP crystals, Second harmonic generation efficiency, Dielectric constant, Dielectric loss

1 Introduction

Ammonium dihydrogen orthophosphate (ADP) crystals have wide applications in non-linear and integrated optics. With several dopants the ADP crystals exhibit several properties. The behaviour of these crystals in radiation fields is also of importance for technology of radiation induced formation of the optical wave guide in this crystal. In recent years, ADP has gained considerable importance because of their important non-linear, ferroelectric, piezoelectric and electro-optic properties. They have attracted the interests of many theoretical and experimental researchers, probably because of their comparatively simple structure and very fascinating properties associated with hydrogen bond system involving large isotope effect. A most conspicuous feature in the development of physics of these crystals is the close interplay between theory and experiments, which makes possible significant progress in the understanding of their microscopic properties.

Crystals with high conversion efficiencies for second harmonic generation are desirable in various fields. With the aim of discovering new useful materials for academic and industrial use an attempt has been made to modify ADP crystals by adding 1 mole % by weight of Nitrite tri acetic acid and EDTA in mother solution of ADP. In the present paper, the SHG efficiency and dielectric studies of ADP crystals containing nitrite tri acetic acid and EDTA have been reported.

2 Experimental Details

2.1 Crystal growth and testing

Single crystals were grown from supersaturated solution at room temperature by natural evaporation process using AR grade samples of ADP, Nitrite tri acetic acid and EDTA. ADP was added with Nitrite tri acetic acid and EDTA separately, each in definite molecular ratio, viz. ADP: X (X reps dopants added in one molar wt ie in 10:1 ratio). All the grown crystals were found to be very stable, colorless and transparent and exhibited scalenohedral (twelve sided polyhedron) morphology. The crystals were characterized using X-ray diffraction and energy dispersive X-ray spectroscopy (EDAX). EDAX data have confirmed the presence of nitrite tri acetic acid and EDTA. Crystals with high transparency were used for SHG and dielectric measurements.

2.2 SHG measurement

The experimental set-up used in the present investigation was similar to the generic one devised by Kurtz. To measure the powder SHG efficiency, samples were derived from the crystals grown with full morphology, which ensure homogeneity of the material. A Q-switched Nd-YAG laser whose output was filtered through 1064 nm narrow pass filter was used for this purpose. The input power of the laser beam was measured to be 6.6 mJ/pulse. Pure ADP was used as reference sample. Both the reference and test samples had uniform particle size (30-50 μm).
The experiment was first carried out in pure ADP and later in ADP added with nitrite tri acetic acid and EDTA. Throughout the experiment the laser power was kept constant.

2.2 Dielectric measurement

The extended portions of the crystals were removed completely and the samples were ground to proper thickness and polished. Each sample was electroded on either side with air-drying silver paste so that it behaved like a parallel plate capacitor. A 4275A, multi frequency LCR meter (Hewlett-Packard) was used to measure capacitance (C) and dissipation factor (D) of the sample as a function of frequency. The dielectric constant (ε) and dielectric loss (tanδ) were calculated from C and D using the relations, $\varepsilon = \frac{Cd}{\varepsilon_0}$ and $\tan\delta = D \varepsilon$

where C is the capacitance of the sample, d the thickness of the sample, A the area of the face in contact with the electrode and $\varepsilon_0$ the permittivity of free space.

3 Results and Discussion

The SHG efficiency of ADP containing nitrite tri acetic acid and EDTA is found higher than pure ADP. For NLO systems to show second order non-linear activity, the additives and the dopants in them have to be macroscopically aligned, and only then there can be increase in efficiency, which has been justified experimentally4-6. The measured SHG signal and efficiency are given in the Table 1.

The variations of dielectric constant (ε) and dielectric loss (tanδ) at room temperature for ADP and ADP containing with nitrite tri acetic acid and EDTA are shown in Figs 1 and 2. It is observed that the dielectric constant (ε) decreases with the increase in the frequency. The dielectric constant of a material is generally composed of four types of contributions, viz ionic, electronic, orientational and space charge polarizations. At low frequencies all polarizabilities are operative hence ε is high. As frequency increases one polarization mechanism after another is frozen out. The first to stop contribution to ε is orientational component, then the ionic and lastly the electronic7-9.

The dielectric loss (tan δ) is due to the resistive component that makes them lossy, so that they dissipate some of the applied ac energy. Tanδ in the present study was found initially to decrease with frequency and later almost a constant over a range of frequencies.

4 Conclusions

Good quality large size optically transparent ADP crystals and ADP crystals with nitrite tri acetic acid and EDTA were grown by slow evaporation

<table>
<thead>
<tr>
<th>Sample</th>
<th>SHG signal 2ω (mv)</th>
<th>Efficiency with respect to ADP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure ADP</td>
<td>9.5</td>
<td>1.0000</td>
</tr>
<tr>
<td>ADP + Nitrite tri acetic acid</td>
<td>12.5</td>
<td>1.315</td>
</tr>
<tr>
<td>ADP + EDTA</td>
<td>16.5</td>
<td>1.7368</td>
</tr>
</tbody>
</table>

Table 1 — SHG efficiency of pure ADP and ADP crystals added with nitrite tri acetic acid and EDTA

Fig. 1 — Variation of dielectric constant with frequency

Fig. 2 — Variation of dielectric loss with frequency
technique. EDAX data has confirmed the presence of impurities in the crystal lattice. ADP crystals with nitrite tri acetic acid and EDTA have shown appreciable increase in SHG efficiency as compared to pure ADP crystals. Enhanced efficiency confirms the better alignment of additives and dopants in the crystal matrix.

It is concluded that ADP is turned out to be useful NLO device material for several reasons. It can be grown easily with suitable habit faces. It is transparent, so that phase matching for second harmonic and frequency mixing process can be achieved well into the visible. Higher efficiencies could be achieved by increasing the intensity of input signal. The values of dielectric constant and dielectric loss decrease with frequency. Large value of dielectric constant at low frequencies in the present study confirms the purity of the sample due to the space charge polarization.

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References