mNA 유기 단결정의 성장, 구조 및 경도에 관한 연구

Study on Growth, Structural and Hardness Properties of Solution Grown mNA Crystals

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Meta nitroaniline (mNA) is a organic NLO crystal which has been extensively investigated by researchers till date not only for its potential for exhibiting SHG (d_{eff} =34 pm/V), EO properties but also for its piezoelectric effects(1). According to available reports mNA single crystals are generally grown by Bridgman technique. Recently optical quality crystals are also grown from super cooled melt. However, mNA crystals grown by this technique has inclusions of 1,3 metanitro benzene due to oxidation of mNA(2). Low temperature solution growth has been widely used for growth of organic materials like POM, NPP, NMBA etc. Hence we adapted solution growth method to grow optical quality single crystals of mNA using acetone as solvent and report the characteristics of solution grown crystals.

Commercially available mNA powder (SRL) was further purified to reduce the impurities. mNA powder was dissolved in acetone (E - Merck grade 99.5+% purity)and recrystallised twice to increase the purity. The recrystallised mNA powder was used for solubility measurement and for crystal growth. Solubility of mNA in acetone has been determined for the temperature range of 35 - 50°C by gravimetric method. The solubility curve for mNA in acetone is shown in the Figure 1. The solubility curve is linear with a positive slope value. The solubility coefficient $(dS/dT)/S_0$ for 313 K is 0.01/K and hence solvent evaporation is followed for growth(3). Single crystals of mNA were grown by slow evaporation of saturated solution of mNA in acetone. Crystals of size 10 x 10 x 5 mm^3 were harvested after a week. The grown crystals are yellowish in colour. The morphology of the grown crystals is quadrilateral in shape with well developed (100) faces. As the grown crystals are slightly hygroscopic in nature, the crystal surface becomes cloudy if kept in open atmosphere over long time exposure. Hence the grown crystals were carefully preserved in saturated hydrocarbon liquids of high molecular weight or in paraffin oil.

X-ray powder diffraction spectrum was recorded with Rich Seifert X-ray diffractometer using CuK_α radiation(1.5418 Å). The observed experimental 2θ peak positions have been compared with the reported JCPDS file which agrees well with the experimental peaks. Vickers hardness was measured for (100) and (001) planes of the grown mNA crystals using Leitz Wetzlar hardness tester. For 25 and 50 g radial cracks were obtained for some indentations and hardness was determined using the relation $H_v=1.8544\ p/d^2$ (kg/mm^2) where p is load (gms) and d is the diagonal length in micrometers. This might be due to the plastic deformation or undue cracks induced in the mNA sample. Since relatively weak van der Waals interaction is responsible for the intermolecular binding of mNA molecules in solid, the mechanical properties of the mNA molecules in solid are rather fragile. However, mNA shows hardness higher other than that of organic crystals like urea[(4)]. Plot of load (P) against Vickers hardness (H_v) is shown in the Figure 2. It was observed that the microhardness number decreases with the increase in load for the given planes. This might be caused the movement of disclocations away from the indentor tip due to the local pressure created at indentor tip and cracks propagate thereby decreasing the resistance and material deforms more. Anisotropy in crystal faces account for different hardness values along the planes. mNA crystals grown by this technique are good candidates for NLO applications.

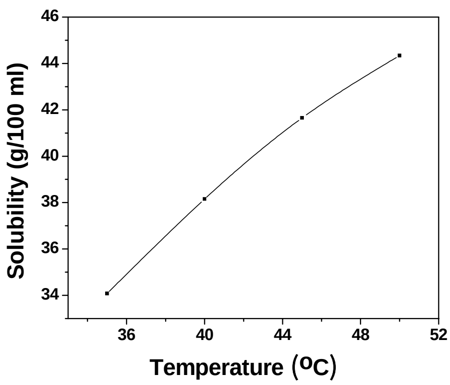

Fig.1 solubility curve for mNA

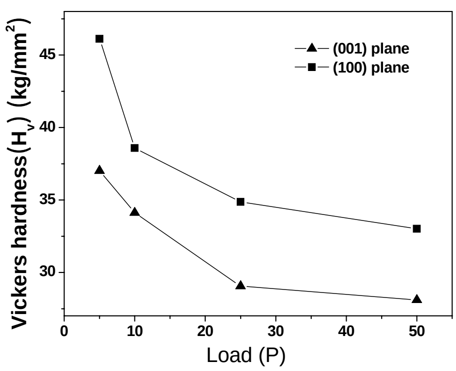

Fig 2. plot of Load(P) against Hardness

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