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The birefringence spectroscopic studies on ferroelectric glycine phosphite (GPI) single crystals

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The ferroelectric glycine phosphite single crystals have been grown from aqueous solution by both conventional and Sankaranarayanan-Ramasamy methods. The modified channelled spectrum method has been adopted for spectral dependence of optical birefringence studies over the wavelength range of 480–620 nm, which show that both the crystals exhibit relatively high birefringence values. The photoluminescence excitation studies were carried out for the grown crystals in a wide wavelength range between 300 nm and 600 nm at 224 K. The crystals were also subjected to scanning electron microscopy analysis in order to determine the ferroelectric domain pattern configuration.

Keywords: *crystal growth; birefringence; semi-organic materials; photoluminescence; SEM*

1. Introduction

Worldwide demand for good quality single crystals for various applications motivates the development of new techniques for the growth of bulk crystals from melt and solutions. The main advantages of solution growth methods are convenience, simplicity and possible avoidance of complex growth apparatus. For practical optical applications, we need crystals which have good transparency in the desired wavelengths, chemical stability and the ability to withstand high optical powers. It is hard to find a material which satisfies all the above-said requirements equally well [1]. Especially, the complexes of many inorganic derivatives and amino acids provide excellent crystals such as triglycine sulphate and L-arginine phosphate, which are accepted for the fabrication of devices [2]. Glycine phosphite (GPI) is a hydrogen bonded ferroelectric single crystal. Many researchers were attracted by the structural property of GPI crystals which was found suitable for high sensitivity pyroelectric sensors at room temperature [3]. GPI crystallizes in the monoclinic symmetry space group P21/a at room temperature [4]. In the past two decades, the studies on X-ray irradiation effects [5], piezoelectric properties [6], and acoustic properties [7] have been reported. Researchers have also suggested substantial scope for dielectric studies [8–10] on GPI crystals. These studies help us to understand the molecular mechanisms of phase transformation and desired possible contribution of the spin lattice reactions. The present communication reports the growth of GPI crystals by slow solvent evaporation and unidirectional Sankaranarayanan-Ramasamy (SR) method and their characterizations. The results are analysed providing a better understanding of the relationships between the molecular and crystal properties.

2. Experimental procedures

All starting materials were of high purity analytical reagents. The GPI has been synthesized by dissolving glycine in aqueous distilled water containing stoichiometric equivalent of phosphorous

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acid. The GPI salt was prepared according to the following reaction:

$$\underset{\text{(Glycine)}}{NH_2CH_2COOH} + \underset{\text{(Phosphorus acid)}}{H_3PO_3} \rightarrow \underset{\text{(Glycine Phosphite)}}{(NH_3CH_2COOH)H_2PO_3} \quad (1)$$

The prepared solution was heated up to 80 °C and then cooled down to 0 °C to obtain GPI in the powder form. GPI salt of high purity was obtained through successive recrystallization process. The purified powder was used as a raw material for single crystal growth. A single crystal of GPI grown from the resulting saturated solution (pH – 3.5) was kept under ambient conditions for isothermal slow evaporation. The evaporation rates were regulated by suitable perforates. Optically transparent GPI single crystals of average dimensions $12 \times 10 \times 10$ mm^3 were harvested from the saturated solution in a span of 20 days. The photographs of conventional GPI crystals are shown in the Fig. 1a. A well faceted crystal obtained by slow evaporation was chosen as the seed crystal with reasonable size to grow a single crystal in SR method. Next, the seed crystal <010> face has been carefully cut, shaped into a disc, polished and then housed at the bottom of an ampoule to impose the growth direction. Then, the ampoule was mounted in a constant temperature bath of 35 °C, which is the optimum growth temperature in SR method according to our experimental observation. The 48 mm in length and 20 mm in diameter single crystal of GPI was harvested from the ampoule within the span of 25 days. The disc shaped specimens of GPI are shown in Fig. 1b.

3. Results and discussion

3.1. Optical birefringence properties

In the past few decades, physicists were interested in the precise measurement of the principle refractive index and the optical double refraction (birefringence) along with their dispersion with wavelength which plays a vital role in the linear and non linear optics [11]. Birefringence dispersion seems to play an important role in many applications of crystals, including retardation plates, polarizers and optical modulators [12]. Many techniques were adopted for the accurate measurement of birefringence of the crystals, which in turn need expensive and highly sophisticated optical instruments as well as large size sample. However, in the present study the modified channel spectrum method (CS) has been employed for quantitative assessment of the optical quality of the grown specimens. It is a simple and indirect method to measure birefringence of crystals even without prior knowledge of refractive index of the crystals. The improved accuracy of birefringence values (close to the prism method) can be obtained by reducing the thickness of the samples to the order of 10^{-4} or 10^{-5} [13]. The values of birefringence have been calculated by finding the absolute fringe order for particular wavelength and computed from the relation:

$$\Delta n = k\lambda/t \quad (2)$$

where λ is the wavelength in nm, t is the thickness of the crystal in mm, and k is the fringe order [14]. The graph of birefringence (∇n) versus wavelength (λ) is presented in Fig. 2. The birefringence value of the conventional grown crystals was found to be 0.063537 at the wavelength 607 nm, and that of the SR method grown crystal was 0.063981 at the wavelength 613 nm, and these values are in close agreement with the published data [15]. From the obtained values it is clear that the birefringence assessments of GPI crystals can be classified as optically negative at 303 K [16].

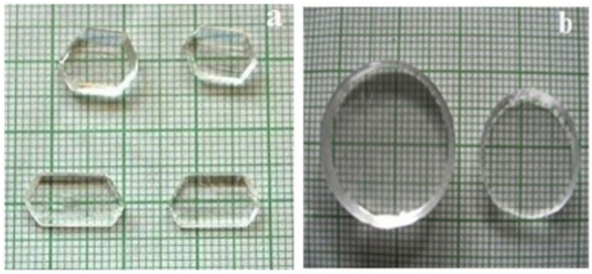

Fig. 1. Photographs of as grown GPI single crystals a) conventional, b) SR method.

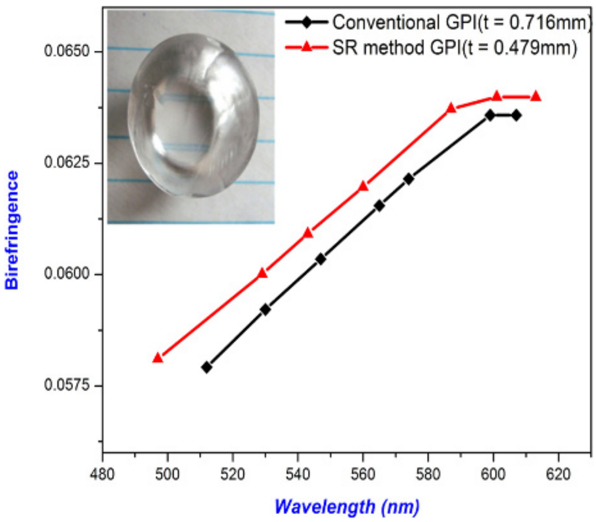

Fig. 2. Dispersion of birefringence versus wavelength of GPI.

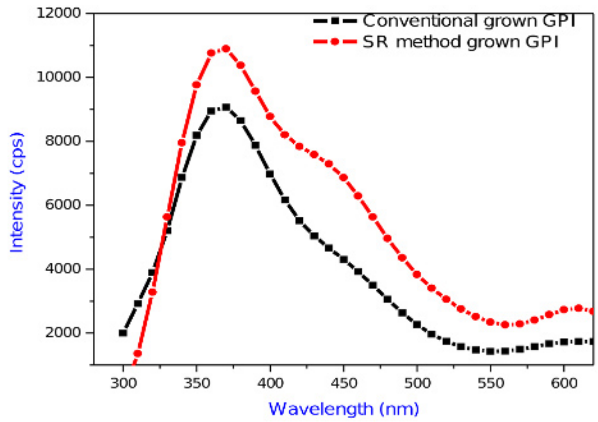

Fig. 3. Photoluminescence spectra of GPI crystals.

3.2. Photoluminescence behavior

Photoluminescence (PL) is a very sensitive tool, as compared to the optical absorption, at the lower concentration of defects, for which optical absorption bands are very weak. Furthermore, PL studies can also identify the presence of defects whose optical absorption bands overlap [17]. In the present study, luminescence behavior of GPI has been studied at 224 K. The as grown single crystals of GPI were scanned between 300 to 600 nm and the excitation wavelength was 250 nm. The luminescence light was collected using a collector assembly and transmitted to the spectrograph through an optical fiber for analysis and detection. The recorded PL spectrum is displayed in Fig. 3. It is clearly seen that the spectrum consists of a single luminescence band, which is rather intense, slightly asymmetric and has its center at 367 nm in the lower wavelength region. Both conventional and SR grown crystal show a strong emission between 360–370 nm for an excitation of 250 nm. It is clearly seen from the plot that the high intensity and shape of the luminescence bands are quite similar for both the crystals. The intensity of emission of SR grown ingot is higher than that of conventional grown GPI crystal. Thus, the result reveals that the GPI crystals have lower concentration of defects than the conventional grown specimen.

4. Ferroelectric domain patterns

SEM has been widely used for several years for the analysis of surface domain structures in ferroelectrics [18]. The as-grown surface of both the crystals were cleaved and introduced into SEM for investigation as quickly as possible, because if the surface to be studied is exposed to the atmosphere for a long time, the internal bias induces a big adsorption and the observation would not be possible. Here, all the investigations were carried out at above 230 K and below 205 K transition temperature on the b-cut plate of the GPI single crystals by using the JEOL model JSM 6390 SEM, and without any metallization of the sample. In order to observe the domain pattern in the static conditions, the primary electron beam, which carried a low probe current $I_p = 3$ pA under a low acceleration voltage $V_a = 20$ kV, was normally incident on an uncoated b-surface in a vacuum of 1.33×10^{-4} Pa. The primary beam having a diameter r_p less than 150 nm scanned the b-surface along the c-axis at a speed $v_p = 16$ cm/s in the photographic scan mode of the SEM. The domains observed on the GPI crystals were aligned perpendicular to c-axis. SEM images show that the brighter parts correspond to the region of negative domain, where the surface potential was lower than that of the surroundings. The relatively dark region is the positive domain region. The SEM images (Fig. 4a,b) show ferroelectric domain patterns of the conventional grown crystals. There is a significant variation in the domain patterns of SR

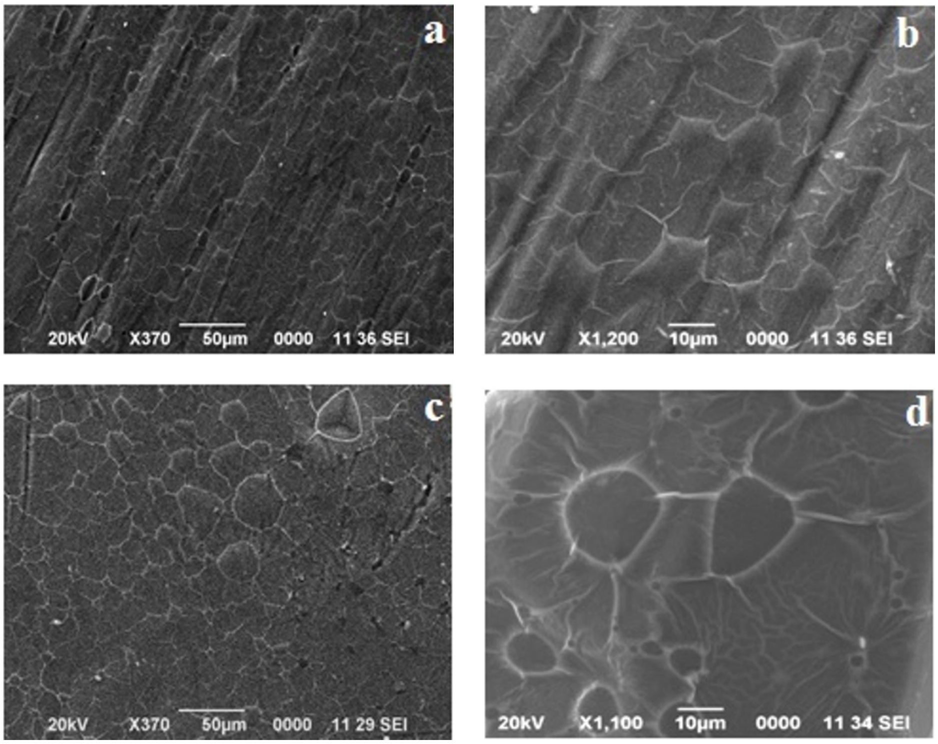

Fig. 4. SEM analysis of domain patterns in GPI crystals; (a) conventional grown at 230 K; (b) conventional grown at 205 K; (c) SR method grown at 230 K and (d) SR method grown at 205 K.

grown crystals (Fig. 4c,d). The domain contrast of the SR grown crystal is better than that of conventional grown crystals, due to the lower number of defects on the surface of the SR grown GPI samples.

5. Conclusion

In conclusion, the ferroelectric glycine phosphite (GPI) single crystals have been successfully grown from aqueous solution by both conventional and Sankaranarayanan-Ramasamy (SR) methods. The improvised channelled spectrum method has been adopted for birefringence measurement of the material, which showed that both the samples were optically negative at room temperature and had relatively high birefringence values of 0.063537 and 0.063981 at the wavelength of 607 nm and 613 nm respectively, compared to the well known ferroelectric KDP crystals. The photoluminescence measurements indicated that the SR grown glycine phosphite crystals had lower defects concentration. The ferroelectric domain configuration of SEM images revealed that the domains were aligned in a similar fashion in both the crystals.

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