

Comment on “Synthesis, growth, structural, spectroscopic, crystalline perfection, second harmonic generation (SHG) and thermal studies of 2-aminopyridinium picrate (2APP): A new nonlinear optical material” [*Solid State Sci.* 14 (2012) 773-776]

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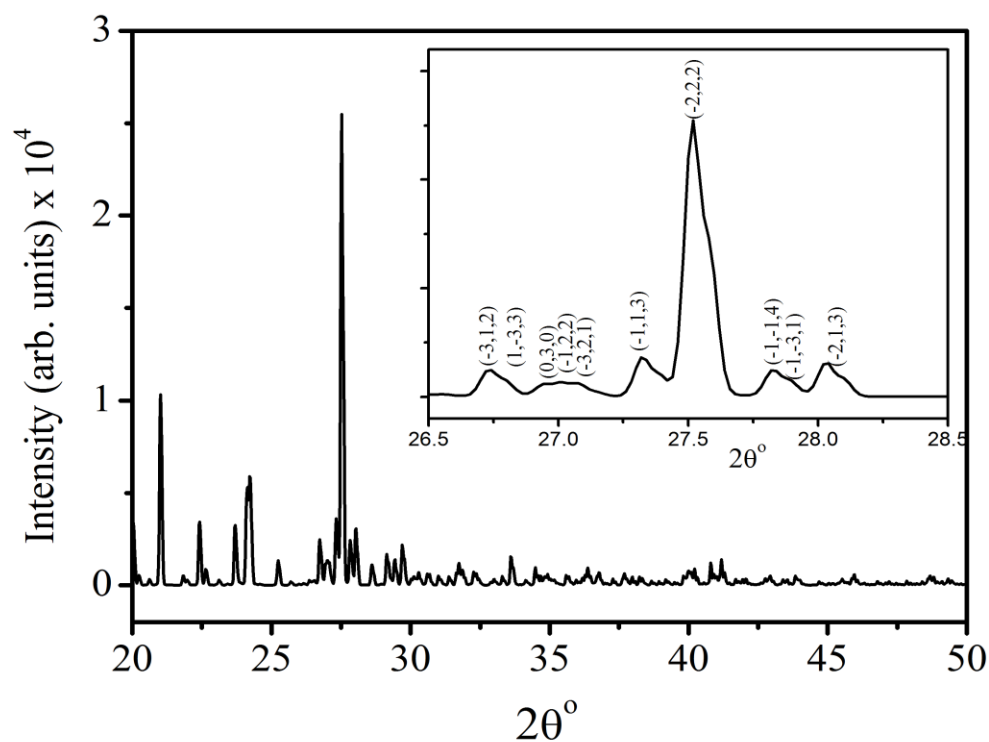
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Graphical Abstract

2-Aminopyridinium picrate is a centrosymmetric solid.



Comment on “Synthesis, growth, structural, spectroscopic, crystalline perfection, second harmonic generation (SHG) and thermal studies of 2-aminopyridinium picrate (2APP): A new nonlinear optical material” [Solid State Sci. 14 (2012) 773-776]

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Abstract

The compound 2-aminopyridinium picrate (2APP) reported by Shkir *et al* (Solid State Sci. 14 (2012) 773-776) is a centrosymmetric solid and not a nonlinear optical material.

Keywords: 2-aminopyridinium picrate; centrosymmetric solid; nonlinear optical material.

Comment

2-Aminopyridinium picrate (2APP) is a solid crystalline material prepared by reacting equimolar amounts of 2-aminopyridine and picric acid in methanol [1]. It is interesting to note that 2APP which is a derivative of a centrosymmetric solid ($P2_1/c$) namely 2-aminopyridine [2] and picric acid a non-centrosymmetric solid [3], crystallizes in the triclinic crystal system in the centrosymmetric $P-1$ space group [1]. To the best of our knowledge, no other polymorphic modification of 2APP crystallizing in a non-centrosymmetric space group other than the $P-1$ form reported by Sivaramkumar *et al* [1] is known till date. Shkir *et al* grew crystals of 2APP following the reported procedure [1] and found the unit cell parameters of their crystals to be in agreement with data in [1] and reported the following in the title paper [4]: „Single crystal X-ray diffractometry analysis revealed that 2APP crystals belong to the triclinic system with space group $P-1$, which is recognized as non-centrosymmetric structure; basic requirement to be an SHG active crystal“. After, incorrectly recognizing the $P-1$ space group as non-centrosymmetric, the authors measured the second-harmonic generation (SHG) efficiency of their 2APP crystals

and observed a SHG signal of 0.15 times of KDP. Based on this, they reported that 2APP is a promising candidate for the fabrication of NLO devices [4]. As it is well documented that the presence of a symmetry center in bulk crystals eliminates the possibility of SHG [5], the authors' designation of nonlinear optical material for 2APP is inappropriate.

The contradiction between the experimental results and the crystal symmetry of 2APP can be explained due to the presence of impurities in 2APP, which cannot be ruled out, as the authors assigned a broad endothermic peak in the TG-DTA thermogram for the evaporation of solvent molecules. In their discussion of high resolution X-ray diffraction analysis of 2APP, the authors mentioned about entrapped solvent molecules. Since the molecular formula of 2APP contains only pyridinium cation and picrate anion and no solvent molecule, the above mentioned results of Shkir *et al* indicates that they were probably investigating a solvated crystal in some of the experiments. A comparison of the X-ray powder pattern of 2APP calculated using cif data of Ref. [1] in Fullprof Suite, with that of the reported pattern [4] indeed indicates that the phase is impure [Fig.1]. The signal at 3423 cm^{-1} in the reported infrared spectrum indicates the presence of -OH group, which is not present in the structure of 2APP but is a constituent of picric acid. The observed SHG signal for 2APP in [4], can thus be attributed to the presence of trace amounts of picric acid, which is a known non-centrosymmetric material crystallizing in the $Pca2_1$ space group [3]. It is pertinent to note that an earlier claim [6, 7] of unusual SHG activity and piezoelectric behavior in another centrosymmetric picrate compound namely glycine picrate has been disproved [8, 9]. The reported SHG activity of glycine picrate compound was unambiguously shown to be due to picric acid impurities [9]. In summary, the compound 2-aminopyridinium picrate described in the title paper is a well known centrosymmetric solid and not a new nonlinear optical material.

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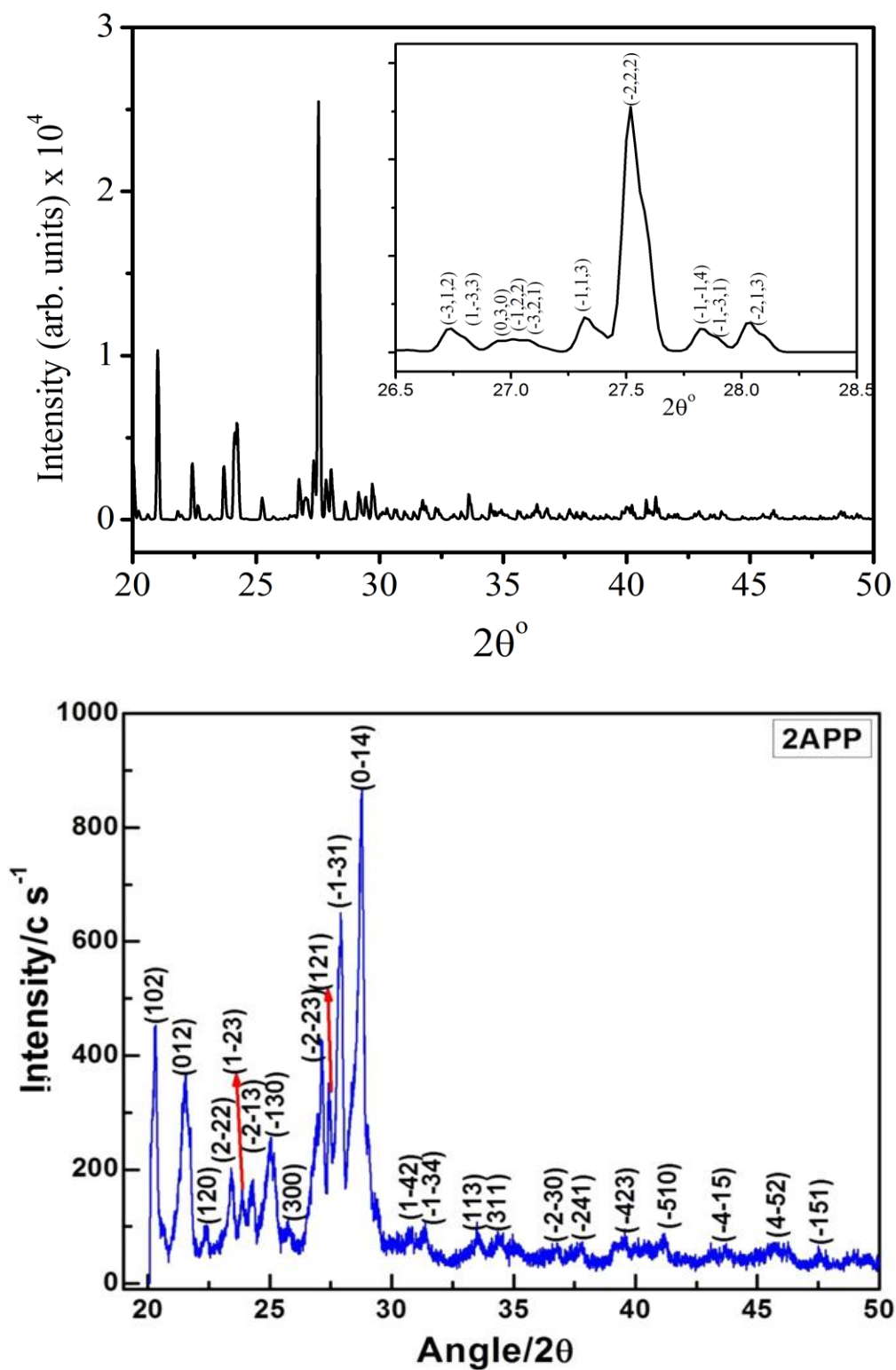


Fig. 1 Comparison of theoretical powder pattern for 2APP (top) with the reported powder pattern in Ref. [4] for 2APP (bottom). 2θ region from 26.5 to 28.5 is expanded, showing the indices as an inset. (Note- For theoretical pattern cif data in Ref [1] was used.)

Highlights

- 2APP is a centrosymmetric solid.
- Reported phase is impure.
- Picric acid impurity is responsible for SHG response.