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Comments on 'Process development and characterization of centrosymmetric semiorganic nonlinear optical crystal: 4-dimethylaminopyridine potassium chloride'

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Highlights

A comment on the title paper is reported

Experimental data reported in the title paper are discussed

4-dimethylaminopyridine potassium chloride is potassium chloride

Abstract

The authors of the title paper [Phys B. Condens. Matter **538** (2018) 199-206) report to have grown 4-dimethylaminopyridine potassium chloride (4-DMAPKC) crystal by slow evaporation solution growth method. In this communication, many points of criticism, concerning the crystal growth, single crystal structure and X-ray powder pattern of this so called 4-DMAPKC crystal are highlighted to prove that the title paper is completely erroneous and the title crystal is potassium chloride.

Keywords: *4-dimethylaminopyridine; potassium chloride; dubious crystal; 4-dimethylaminopyridine potassium chloride; erroneous paper*

Comment

It is well documented in the literature that an essential prerequisite for nonlinear optical (NLO) activity is that any material should crystallize in one of the twenty noncentrosymmetric crystal classes. In view of this centrosymmetric crystals cannot be nonlinear optical (NLO) materials. Hence a paper titled '*Process development and characterization of centrosymmetric semiorganic nonlinear optical crystal: 4-dimethylaminopyridine potassium chloride*' [1] attracted our attention. The paper was perused to understand the process development for a so called centrosymmetric nonlinear optical crystal *4*-dimethylaminopyridine potassium chloride (4-DMAPKC) hereinafter referred to as **I** to avoid use of a long name and a strange code. The scrutiny of the paper revealed several inconsistencies showing that **I** is a dubious material and is an example of an incorrectly identified crystal as shown below.

According to the authors the title crystal was grown by slow evaporation method by taking 4-dimethylaminopyridine and potassium chloride in 1:1 ratio in water. The scheme of the reaction showing coordination of K^+ ion to the pyridine N and a link between one H atom of the methyl group of dimethylamine substituent with the amino N of another 4-dimethylaminopyridine in **I** is not as per the known chemistry of potassium which is an oxophilic metal. Based on a single-crystal X-ray diffraction analysis a ridiculously low unit cell volume of 29.0Å^3 was reported for **I**, which is supposed to contain eleven non-hydrogen atoms in its structure. The dubious nature of the single crystal work is further revealed by the following claim about the space group "*It is realized that the grown 4-DMAPKC crystal belongs to cubic system with centrosymmetric space group $P2_1/a$*". In addition to an incorrect space group representation, the authors did not realize that such cell volumes are impossible for any crystal. However, they made the following remarkable claim '*Addition of KCl in 4-DMAP shows that there is change in cell volume of 4-DMAPKC (29.0 Å^3) confirms the*

inclusion of potassium in to 4-DMAP crystal lattice with change in the lattice parameters value'. The reported X-ray powder pattern is even more unusual with just two signals at around 2theta values of 26 and 56^{o} assigned for the reflections (2 0 0) and (4 0 0) respectively. However, the authors reported, '*The sharp and well defined peaks at 2θ angles identified in the XRD pattern confirm the crystalline nature of the crystal.*' The authors explain the observation of SHG as follows: *In the grown 4-DMAPKC centrosymmetric crystal, due to the hydrogen bonding between methyl group of 4-DMAPKC to adjacent molecules, parallel alignment of dipole moment between organic 4-DMAP with inorganic potassium chloride, symmetry breaking between the monolayer interfaces of grown 4-DMAPKC crystal, intramolecular charge transfer between 4-DMAP ligand to metal (LMCT) and asymmetric distribution of π-electron cloud density of 4-DMAPKC are responsible for SHG.* However, this explanation is unacceptable as it is unscientific.

In the IR spectral discussion, the authors assigned a peak at 3445 cm^{-1} for N-H stretching vibration. However, no N-H group is present in the structure. A signal at 547 cm^{-1} assigned for the K-N stretching vibration actually appears to be electronic noise. No reports of any compounds of 4-dimethylaminopyridine with *s*-block metals including potassium has appeared in the literature to date. The dielectric constant measured at 50 Hz is more than 2000. It is noted that in the range from 1 kHz to 5 MHz, it is over 200. In non-ferroelectric crystals such values are unbelievably large. The reported dielectric loss (tanδ) at 50 Hz is 10 which means that the imaginary part of the complex dielectric constant is 10 times larger than its real part. Even at higher frequencies, tanδ is around 0.7. Such high tanδ values can be due to measurements performed in a humid atmosphere or measurement errors which appears to be more likely in the present case. All the above discussed unusual experimental results do not in any way correlate with the title crystal **I** and do not provide any clue whatsoever as to what material was actually obtained by the authors in their crystal growth reaction. In

another publication on a so called 4-dimethylaminopyridine potassium chloride 2-aminopyridine crystal **II** abbreviated by a very long code (4-DMAPK2AP) [2] the same authors reported the unit cell parameters of **II**, which perfectly match with the cell parameters of KCl indicating that the authors obtained only KCl and not any (4-DMAPK2AP). According to authors, the crystal **II** was obtained by slow evaporation of a solution containing potassium chloride, 4-dimethylaminopyridine and 2-aminopyridine. Regrettably **II** is also a dubious crystal like **I**. In view of this we believe that in the present case for compound **I** the authors must have obtained KCl and the absence of 2-aminopyridine has in no way affected the product formation.

We explain the very unusual experimental claims reported in the commented paper as follows: The authors of [1] assumed that slow evaporation of an aqueous solution containing potassium chloride and 4-dimethylaminopyridine will result in the formation of a so called 4-dimethylaminopyridine potassium chloride crystal **I** due to incorrect interpretation of the data. However, the crystal obtained by them is actually KCl due to fractional crystallization. It is regrettable that such a manuscript was published in a peer reviewed international journal.

In summary, we have proved that **I** is a dubious material and the title paper is completely erroneous.

References

[1] J. Johnson, R. Srineevasan, D. Sivavishnu, Process development and characterization of centrosymmetric semiorganic nonlinear optical crystal: 4-dimethylaminopyridine potassium chloride, *Physica B: Condensed Matter* **538** (2018) 199-206.

[2] J. Johnson, R. Srineevasan, D. Sivavishnu, Synthesis, growth and characterization of 4-dimethyl-aminopyridine potassium chloride 2-aminopyridine: semiorganic nonlinear optical crystal, Chemistry Reports **1** (2018) 20-27.