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Comments on the paper "Customizing optical and dielectric traits of ammonium dihydrogen phosphate (ADP) crystal exploiting Zn^{2+} ion for photonic device applications"

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Highlights

Growth of Zn^{2+} ion influenced ammonium dihydrogen phosphate (Zn-ADP) is critiqued

Experimental data are discussed

Zn-ADP crystal is a dubious material

Abstract

The authors of the title paper (*Chin J Phys* **63** (2020) 70-77) claim to have grown a Zn^{2+} ion influenced ammonium dihydrogen phosphate (Zn-ADP) crystal by the slow solvent evaporation technique. In this comment, many points of criticism, concerning the crystal growth and characterization of the so-called Zn-ADP crystal are discussed to prove that it is a dubious material and the title paper is erroneous.

Keywords: ammonium dihydrogen phosphate; zinc; Zn^{2+} ion influenced ammonium dihydrogen phosphate; dubious crystal

Introduction

Recently I chanced to read a paper by Baig *et al*. [1] published in the *Chinese Journal of Physics*. The abstract of [1] revealed that the work is on a so-called Zn^{2+} ion influenced ammonium dihydrogen phosphate crystal referred to by the code Zn-ADP. Ammonium dihydrogen phosphate (ADP) is a well-known solid [2,3] in the scientific literature unlike '*Zn^{2+} ion influenced ADP crystal*' which appeared to be an unusual terminology. In view of this I perused the title paper to understand the meaning of '*Zn^{2+} ion influenced ADP crystal*' but noted that the molecular composition of Zn-ADP was not reported in the entire paper; regretfully the reported results do not meet scientific standards. In the following comment the scientific inconsistencies are described to prove that Zn-ADP is a dubious material.

A so-called Zn^{2+} ion influenced ammonium dihydrogen phosphate is a dubious crystal

A perusal of the introduction reveals that since no researcher has reported the effect of Zn^{+2} on various characteristics of ADP crystal, the authors decided to grow for the first time a so-called Zn^{2+} ion influenced ammonium dihydrogen phosphate (Zn-ADP) crystal. A perusal of the experimental details it is noted that authors dissolved AR grade ammonium dihydrogen orthophosphate (ADP) salt in 100 ml of double distilled water to prepare saturated solution of ADP. To facilitate the influence of Zn^{2+} ion on ADP crystal authors added 1 mol of zinc chloride salt to the beaker containing the saturated solution of ADP. Instead of reporting details of the quantities of reagents employed for the crystal growth and percent yield of the final crystalline product, authors mentioned that the solution was placed on the stirrer for six hours for homogeneous mixing and "*the zinc chloride mixed ADP solution*" was filtered using the No. 1 Whatman filter paper. Although it is not clear what "*zinc chloride mixed ADP solution"* means, the authors mentioned, "*The filtrate of Zn^{2+} influenced ADP (Zn-ADP) crystal has been kept in constant temperature water bath maintained at 35 °C. The Zn-ADP crystal of dimension 10 × 07 × 05 mm^3 is ..*" Despite the absence of quantities of reagents it is noted that a saturated solution of ADP was prepared in 100 ml. Based on the solubility of ADP (44 g/dL at 30°C) this amounts to 0.38 mole to which a mole of $ZnCl_2$ was added. Although, it is not clear why

ADP:Zn^{+2} ratio was taken as 1:2.6. However, it is not explained, why the reaction of Zn^{+2} with ADP (equation 1) did not result in the formation of the less soluble bis(hydrogen phosphate) of zinc [4] or other insoluble compounds like $Zn_3(PO_4)_2$ or $Zn(NH_4)(PO_4)$ which are known to form in aqueous solutions containing, zinc(II), ammonium and hydrogenphosphate ions [5].

$$2(NH_4)(H_2PO_4) + ZnCl_2 \rightarrow Zn(H_2PO_4)_2 + 2\ (NH_4)Cl \quad \ldots (1)$$

Although it appears interesting to note that equation 1 resulted in the formation of a so-called Zn^{2+} ion influenced ammonium dihydrogen phosphate crystal abbreviated by the code (Zn-ADP), the lack of sufficient experimental details like makes it tough for other researchers to perform this experiment to get reproducible results. The so-called Zn-ADP crystal was studied by EDS analysis to determine the %Zn in Zn-ADP as 15.53% (Table 1). Based on this the authors declared, "*The obtained concentration of Zn may be adequate to facilitate change in various properties of ADP crystal*", without taking into consideration that the experimental percentages (which do not add up to 100%) are not in agreement with the formulae of either pure ADP or zinc bis(dihydrogen phosphate). Although it has been pointed out that use of elemental analytical data from EDS experiment is an inappropriate method for compound characterization [6], it is only unfortunate that this method was used to characterize the so-called Zn-ADP crystal.

Table 1. Elemental analytical data of pure ADP, zinc bis(dihydrogen phosphate) and so-called Zn-ADP

Name	Elemental Composition	Formula Weight	%H	%N	%O	%P	%Zn	Total %
Pure ADP $(NH_4)(H_2PO_4)$	H_6NO_4P	115.04	5.27	12.18	55.63	26.92	0.0	100.00
zinc bis(dihydrogen phosphate)	$H_4O_8P_2Zn$	259.36	1.56	0.0	49.35	23.88	25.21	100.00
So-called **Zn-ADP**[*]	Not given	--	--	25.62	23.10	31.78	15.53	96.03[#]

[*] Experimetal % from EDS study; [#] experimental data do not add up to 100% and hence questionable

In addition to the EDS experiment authors reported unit cell data determined at room temperature for the pure and Zn-ADP crystal. According to authors, "*The recorded data reveals that the pure and Zn-ADP crystal inhibits the tetragonal crystal structure belonging to the space group domain of I42*d. *It is notable that the cell parameters of ADP crystal are slightly perturbed which gives the evidence of being influenced by* Zn^{2+}". An inspection of the data (without any esd) indicates that the volume of the

Zn-ADP crystal is 432.0 $Å^3$ which is 5.8 $Å^3$ more than that of pure ADP. Although, it is not clear as to why authors consider a small change in volume as an evidence for being influenced by Zn^{+2}, the aim appears to be to report that the crystal obtained is ADP. The reporting of nearly same unit cell parameters for the Zn-ADP contradicts the EDS analysis since the unit cell parameters refers to an ADP cell while the elemental analytical data indicates that the compound cannot be ADP.

The explanation for the contradictory data is due to characterization of materials based on an incorrect assumption namely stirring 1 mole of $ZnCl_2$ with 100 ml of saturated ADP solution will result in a so-called Zn^{2+} ion influenced ADP crystal. The observed presence of Zn in EDS study which does not match for ADP can be explained to a mixture of compounds namely ADP and a phosphate salt of zinc. There is no explanation whatsoever for the non-incorporation of chloride in the Zn-ADP crystal, the less than 100 % total, the charge imbalance due to incorporation of divalent metal (Zn^{+2}) cation in a compound containing monovalent $(NH_4)^+$ cation. The formation of only so-called Zn^{2+} ion influenced ADP crystal without the formation of other zinc containing products like zinc bis(dihydrogen phosphate), zinc ammonium phosphate etc. is totally unacceptable. The study of properties of an improperly characterized solid does not make any scientific sense especially the claim that the Zn-ADP crystal exhibited an second harmonic generation SHG response of 3.15 times KDP. For such a result to be acceptable, the compound synthesis should be reproducible and the chemistry of the synthesis explainable. Without a proper scientific explanation for the increased SHG response, this claim is meaningless. Although several good examples of experimental characterization of dihydrogen phosphate based materials have been published in the literature [2,3,7], the title paper cannot be considered in this category because the presentation of the results in [1] do not meet scientific standards. It is quite unfortunate that such a paper was published in a peer-reviewed international journal. With such contradictory data, the grown crystal should only be declared as a dubious material and not any Zn^{2+} ion influenced ammonium dihydrogen phosphate (Zn-ADP) crystal. In summary, I hope that this comment will bring to an end publication of reports claiming to have grown ADP crystals influenced by some metal ions or organic molecules.

Declaration of interest: None

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