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Comments on "Growth and characterization of tris thiourea magnesium zinc sulphate single crystals" by Bhuvaneswari et al, Optik 126 (2015) 3731-3736

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Abstract

The authors of the title paper report to have grown a tris thiourea magnesium zinc sulphate (TTMZS) single crystal for the first time. In this communication, many points of criticism concerning the synthesis, crystal growth and characterization are highlighted, to prove that the so called TTMZS is not a new nonlinear optical material but a dubious crystal.

Keywords: tris thiourea magnesium zinc sulphate; crystal growth; sulfatotris(thiourea)zinc(II); dubious crystal;

Comment

A recent paper by Bhuvaneswari et al [1] reporting on the growth of a so called tris thiourea magnesium zinc sulphate (TTMZS) single crystal attracted my attention in view of the isolation of a thiourea containing bimetallic (Mg(II) / Zn(II)) compound. The authors reported that this so called TTMZS was synthesized by dissolving thiourea, magnesium sulphate heptahydrate and zinc sulphate in 3:0.25:0.75 ratio in water according to the following reaction scheme.

$$3[CS(NH_2)_2] + MgSO_4 \cdot 7H_2O + ZnSO_4 \rightarrow MgZn[CS(NH_2)_2]_3SO_4 \cdot 7H_2O \qquad .. (1)$$

The confusion about the title crystal begins with a charge imbalance in the proposed formula $MgZn[CS(NH_2)_2]_3SO_4 \cdot 7H_2O$ in view of the presence of a single sulphate for the two bivalent metals Mg and Zn. Since the authors have employed Mg:Zn salts in 0.25:0.75 ratio, they assumed that TTMZS contained $Mg_{0.25}Zn_{0.75}$ per sulphate which they did not indicate. However there is no valid scientific proof for the presence of Mg and Zn in 1:3 ratio excepting their claim, '*The presence of metals such as magnesium zinc, sulfur, nitrogen, etc. in grown crystal was confirmed from EDAX* *spectrum*'. The authors did not take into consideration that a physical mixture of thiourea, $ZnSO_4$ and $MgSO_4$ can also show the presence of the same elements in an EDAX study. Srinivasan and Narvekar [2] have demonstrated with examples that the mere presence of a few elements in an EDAX study is not an acceptable evidence for the proposed molecular formula of a solid. The TTMZS crystal should be considered as one more example for the inappropriate use of EDAX.

Based on a DTA curve (referred to as DTA spectrum by authors) it was reported in thermal studies '*The absence of weight loss up to 100 °C confirmed the absence of water molecule in TTMZS crystal during the crystallization process'*. This adds more confusion because the crystal growth reaction is supposed to have resulted in a product containing seven water molecules ($7H_2O$) for TTMZS crystal. The single crystal X-ray result does not in any way help to resolve the confusion.

The authors reported only the unit cell parameters and the space group as $Pca2_1$ but did not refine the crystal structure (Table 1). A cell volume of 1344 Å^3 which is slightly less than the expected value (1354.80 Å^3) for sulfatotris(thiourea)zinc(II) $[Zn(CS(NH_2)_2)_3(SO_4)]$ [3] also known by the name tris(thiourea)zinc(II) sulphate, was reported for TTMZS, probably to show that the replacement of Zn(II) by Mg(II) has resulted in a slight reduction in the cell volume. However the authors chose an incorrect value because the reported volume is about two and half times more than the expected value of 545.67 Å^3 for the given *a*, *b*, *c* values of the cell. In the absence of a CIF file, the single crystal work cannot be considered as reliable and in the present case the unit cell measurement appears questionable in view of the volume discrepancy. One wonders if any cell was really measured.

Table 1. Unit cell data of a so called tris thiourea magnesium zinc sulphate (TTMZS) and sulfatotris(thiourea)zinc(II)

Compound	*Space group*	*a* (Å)	*b* (Å)	*c* (Å)	V (Å^3)	Ref
TTMZS	$Pca2_1$	15.572	6.315	5.549	**1344**$^{\#}$	1
$[Zn(CS(NH_2)_2)_3(SO_4)]$	$Pca2_1$*	11.1738(2)	7.8011(10)	15.5424(2)	1354.80	3

$^{\#}$ **Incorrect** volume (calculated volume is 545.67 Å^3); *Space group from structure determination

The above mentioned discussions reveal that the authors formulated TTMZS not based on scientific interpretation of the experimental data but based on an incorrect assumption that use of thiourea,

$MgSO_4 \cdot 7H_2O$ and $ZnSO_4$ in 3:0.25:0.75 ratio in a crystal growth reaction will result in the formation of $MgZn[CS(NH_2)_2]_3SO_4 \cdot 7H_2O$. The assignment of the non-centrosymmetric $Pca2_1$ space group without the Flack parameter for TTMZS appears to be to show that the space group of $[Zn(CS(NH_2)_2)_3(SO_4)]$ is retained. However the authors did not take into account that for such an assumption to be true, Mg(II) should form a four coordinate compound of formula $Mg[CS(NH_2)_2]_3SO_4$ isostructural with sulfatotris(thiourea)zinc(II). In $Zn[CS(NH_2)_2]_3SO_4$ the central metal is coordinated to S atoms of three terminal thiourea and an O atom of sulphate and exhibits a $\{ZnS_3O\}$ coordination sphere. The authors are unaware that Mg(II) being an oxophilic metal with preference for six coordination, does not bind to S-donor ligands like thiourea. No structurally characterized Mg-thiourea complex is reported in the Cambridge Database till date [4]. The non formation of any thiourea compound of Mg(II) has been demonstrated by proving that a so called 'thiourea urea magnesium chloride' is actually thiourea [5].

Since Mg(II) cannot bind to thiourea to form any $Mg[CS(NH_2)_2]_3SO_4$ type of crystal, it is of interest to know the exact nature of the TTMZS. In an earlier paper from our laboratory, it was shown that the reaction of thiourea, urea and zinc sulphate in 1:1:1 ratio results in the formation of only sulfatotris(thiourea)zinc(II) crystal due to the reaction of one third of zinc sulfate with all thiourea and the unreacted (two thirds) zinc sulphate and urea remaining in solution. In view of the facile formation of only the tris(thiourea) compound viz. $Zn[CS(NH_2)_2]_3SO_4$ irrespective of the amounts of $ZnSO_4$ and thiourea used, and the oxophilic nature of Mg(II), it is expected that the authors should have got only $Zn[CS(NH_2)_2]_3SO_4$ crystal. In order to verify this, a reinvestigation of the crystal growth of TTMZS was performed using thiourea, magnesium sulphate heptahydrate and zinc sulphate in 3:0.25:0.75 ratio, which resulted in the formation of sulfatotris(thiourea)zinc(II) $Zn[CS(NH_2)_2]_3SO_4$ crystal. The formation of this crystal can be evidenced from the reported IR spectrum which is in agreement with that of $Zn[CS(NH_2)_2]_3SO_4$. Unfortunately, the unit cell of TTMZS did not match with the cell of $Zn[CS(NH_2)_2]_3SO_4$ in view of a questionable measurement. Considering all the above mentioned points the TTMZS single crystal cannot be considered as a new material but should be declared as a NEW “dubious” crystal.

In summary it is shown that a so called tris thiourea magnesium zinc sulphate (TTMZS) single crystal is not a new NLO material but a dubious crystal.

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