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On the influence of *L*-threonine on thiourea and urea on *L*-threonine

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Abstract

We show that the papers on "*L*-threonine doped thiourea" (Thilakavathi et al., Materials Research Innovations 20 (2016) 254-258) and on obtaining a compound "urea *L*-threonine" (Jaikumar and Kalainathan, Crystal Research Technology 43 (2008) 565-571) are completely erroneous.

Keywords*: L-threonine; thiourea; urea; L-threonine doped thiourea; urea L-threonine; dubious crystal*

Comments

"L-threonine doped thiourea"

The authors of [1] report on growth and characterization of an organic nonlinear optical material namely thiourea doped by *L*-threonine and claim to have grown the thiourea crystal doped with 1 mol. % and 3 mol. % *L*-threonine. However, repeated recrystallization made by the authors makes the above values uncertain. A priori it is possible the formation of a compound "thiourea *L*-threonine", which must be non-centrosymmetric due to the presence of optically active *L*-threonine in the structure. Moreover, one may assume that doping can change the symmetry due to changing of phase transition temperature. However, doping with small quantity of *L*-threonine, which does not change the symmetry of thiourea cannot make it "an organic nonlinear optical material". The authors of [1] report powder XRD diagrams of

pure thiourea (TU) and "doped with 1 mol. % and 3 mol. % *L*-threonine", which are quite similar and measured cell parameters without indication of the errors of the measurements and determination of space groups (see Table 1).

Table 1. Unit cell parameters of pure thiourea (TU) and so called *L*-threonine-doped thiourea.

Sample	*a* (Å)	*b* (Å)	*c* (Å)	α=β=γ	System, s.g.	Ref
TU	7.8585	8.4850	5.7124	90°	orthorhombic	[1]
"1mol%"	7.8118	8.413	5.634	90°	orthorhombic	[1]
"3mol%"	7.7797	8.3994	5.5576	90°	orthorhombic	[1]
TU	7.655(7)	8.537(7)	5.520(7)	90°	*P*nma	[2]

In doing so, the authors of [1] additionally claim that "*Thiourea finds widespread use as frequency doublers in laser applications*" without any citations to substantiate this statement. Meanwhile it is well known that thiourea having interesting properties at lower temperature, however, has centrosymmetric structure at room temperature (space group *P*nma at 293K [2]) and therefore cannot display nonlinear optical properties at room temperature. So, the conclusions of the authors on "an organic nonlinear optical material" are not scientifically supported and the paper is to be declared erroneous.

"Urea L-threonine"

The authors of [3] claimed on growing a new nonlinear optical material "urea *L*-threonine", which was obtained from an aqueous solution containing equimolar quantities of urea and *L*-threonine by slow evaporation at room temperature and successive recrystallization.The authors of [3] used various characterization methods, but have not determined its crystal structure. The authors found that the "urea *L*-threonine" has orthorhombic symmetry with cell parameters: *a*=2.5736Å, *b*=7.7448Å, *c*=13.6328Å, α=β=γ=90° and compared these parameters with that of *L*-threonine [4]: *a*=13.611Å, *b*=7.738Å, *c*=5.144Å, α=β=γ=90°, space group $P2_12_12_1$, Z=4 in order to show that the unit cell of *L*-threonine differs from that of

"urea *L*-threonine". In fact these data cannot be correct, because the unit cell volume of orthorhombic "urea *L*-threonine" $V = a.b.c = 271.73$ Å^3 cannot be almost half of unit cell volume of *L*-threonine $V = a.b.c = 541.8$Å^3. Actually the value of the parameter "*a*" should be doubled and interchanged with parameter "*c*". This shows that the "urea *L*-threonine" actually is *L*-threonine. The provided TG and DSC curves of "urea *L*-threonine" well correspond to respective curves of *L*-threonine [5], however, the endothermic effect of decomposition was called exothermic in [3]. Determination of the crystal structures would avoid mistakes [6].

In summary, we showed that "*L*-threonine doped thiourea" [1] is centrosymmetric thiourea and therefore cannot be "an organic nonlinear optical material" and "urea *L*-threonine" [3] is not "a new second order nonlinear optical crystal" but is the well-known *L*-threonine.

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