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Letter to the Editor

Comments on "Synthesis and characterization of gadolinium tungstate doped zinc oxide photocatalyst, *Indian J Chem*, 56A (2017) 50-56"

Dear Editor:

The title paper by Thirumalai *et al.*[1] reporting on the hydrothermal synthesis of a so-called 5 wt% Gd_2WO_6 doped zinc oxide (**1**) and its photocatalytic activity attracted my attention in view of my interest on doped crystalline materials[2,3]. Although the reason for the choice of the monoclinic form of Gd_2WO_6 for doping into the crystal structure of hexagonal zinc oxide is not clear, the synthetic methodology especially the stoichiometry of reagents employed and the methods of characterization do not provide any credible evidence whatsoever for the preparation of **1**. In the following comment, it is shown that **1** is a doubtful solid and the title paper is erroneous.

Can monoclinic gadolinium tungstate be doped into the hexagonal zinc oxide?

Zinc oxide represented by the chemical formula ZnO is a wide-bandgap semiconductor and has been the subject of many research investigations by several groups. A comprehensive review of ZnO materials and devices has appeared in the literature[4], which does not make any mention of Gd_2WO_6 doped ZnO materials. Since the metal atoms in Gd_2WO_6 exhibit higher oxidation states namely Gd(III) and W(VI) unlike the Zn(II) in ZnO, it is not clear if Gd_2WO_6 doping into ZnO will result in the formation of *n*-type or *p*-type semiconductor. The authors have reported that the hydrothermally prepared zinc oxide crystallizes in the hexagonal wurtzite structure (space group $P6_3mc$) while the Gd_2WO_6 dopant is monoclinic (space group *I2/a*). In addition to a space group mismatch, the discussions in the title paper do not reveal which sites of ZnO are occupied by the Gd_2WO_6 dopant or alternatively the structural features of Gd_2WO_6 which favour doping in ZnO lattice. A dopant is a trace impurity element that is inserted into a substance (in very low concentrations) to alter the electrical or optical properties of the substance. Further Wikipedia states that in the case of crystalline substances, the atoms of the dopant very commonly take the place of elements that were in the crystal lattice of the base material. From the above given discussion it appears that the structural features of the host material and the dopant have not been given due consideration to know if Gd_2WO_6 can be incorporated into the crystal structure of ZnO.

A perusal of the experimental details reveals that the ratio of Gd:W:Zn reagents used for the synthesis of a so called 5 wt% Gd_2WO_6 doped zinc oxide **1** is 1:1:8. The reason for the use of $Gd(NO_3)_3 \cdot 5H_2O$ and $Na_2WO_4 \cdot 2H_2O$ in equimolar amounts instead of the desired 2:1 mole ratio for the formula Gd_2WO_6 is not very clear. Although the preparation of Gd_2WO_6 in alkaline medium by addition of NaOH appears simpler compared to a recently reported synthesis of Gd_2WO_6 , which involves heating of Gd_2O_3 and WO_3 at high temperature[5], there is no precedence or literature report suggesting formation of only Gd_2WO_6 and no $Gd(OH)_3$ in an alkaline medium. Despite the choice of a very unusual mole ratio of the reagents namely 0.04 mole of Zn for each 0.05 mol of Gd or W for a 5 wt% Gd_2WO_6 doped zinc oxide, authors were confident of having obtained a so called Gd_2WO_6 doped zinc oxide based on a comparison of X-ray powder pattern and incorrectly claimed the pattern to be due to the monoclinic phase of Gd_2WO_6.

Based on an EDS study of elemental composition the authors declared '*EDS spectrum confirms the*

Table 1 – Theoretical wt% of Zn, O, Gd and W in pure and Gd_2WO_6 doped zinc oxides

Name	Formula	M. wt.	Zn (%)	Gd (%)	W (%)	O (%)	Total (%)
Pure Zinc oxide	ZnO	81.39	80.34	---	---	19.66	100
Pure Gd_2WO_6	Gd_2WO_6	594.34	---	52.92	30.93	16.15	100
5 wt% Gd_2WO_6 doped zinc oxide	Gd_2WO_6-ZnO[a]		76.32 (38.46)[b]	2.65 (5.03)[b]	1.55 (26.39)[b]	19.48 (30.12)[b]	100 (100)[b]

[a] 100 g of material contains 95 g ZnO and 5 g of Gd_2WO_6.
[b] Values in bracket are the experimental values reported in Ref. 1.

purity of the prepared catalyst, since there is no peak for any other elements'. However the authors are unaware that the mere observation of a few elements in an EDS study is no valid scientific proof for the purity of a compound. Examples of improperly characterized compounds due to an incorrect interpretation of the EDS data have been reported in recent literature[6, 7]. The title paper is one more example showing that EDS is an inappropriate method to formulate compounds based on elemental composition data as can be evidenced by a comparison of the experimental % with the value expected for the proposed formula (Table 1).

By definition, a 5 wt% Gd_2WO_6 doped zinc oxide means a 100 g material containing 95 g of ZnO and 5 g of Gd_2WO_6. For pure ZnO the expected wt% of Zn is 81.39 and for a material containing only 95% ZnO the expected weight % of Zn is less than 81.39 and for **1** this is found to be 76.32% (Table 1) which is almost twice that of the value (38.46%) obtained by the authors indicating the questionable nature of **1**. It is not clear if authors consider **1** as 5 wt% Gd_2WO_6 doped zinc oxide due to observation of 5% Gd in the EDS study. The % W (26.39) is five times more than the % Gd (5.03) content which is unacceptable because the weight % of W expected is less than for Gd in Gd_2WO_6. The unusually small % of Zn and very high values % of Gd, W and O in the EDS study are not in agreement with the calculated values showing that **1** is not 5 wt% Gd_2WO_6 doped zinc oxide but is a dubious material. In view of the improper characterization of the so called 5 wt% Gd_2WO_6 doped zinc oxide, the properties of such a material viz. photocatalytic activity does not make any sense and hence these results do not merit any further discussion.

In summary, it is shown that the recently reported 5 wt% Gd_2WO_6 doped zinc oxide is a doubtful material.

References

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Response to the Comments

We reported the preparation of 5% Gd as gadolinium tungstate loaded ZnO. In most of the papers, we referred, loading is also termed as doping.

In the preparation of ZnO with our reported procedure, we got 2.7 g of ZnO. Gd (5 wt%) is 0.135 g. So, we had taken 0.371 g of $Gd(NO_3)_3.5H_2O$ which is equivalent to 0.135g Gd. (In the referred paper, 0.243g (approx. equiv. to 3 wt%) is mentioned by mistake and may be corrected). Gd_2WO_6 was prepared using the $Gd(NO_3)_3.5H_2O$ and $Na_2WO_4.2H_2O$.[1] This Gd_2WO_6 suspension was added during the formation of zinc oxalate from $Zn(NO_3)_2.6H_2O$ and oxalic acid. Then ZnO was formed after hydrothermal treatment and calcination. So, Gd_2WO_6 may have been well dispersed in the lattice of ZnO. It is not the sample mixing of Gd_2WO_6 and ZnO.

Hydrothermal treatment gives good morphological structures. XRD pattern shows the presence of wurtzite structure of ZnO (JCPDS No.36-1451) and monoclinic structure of Gd_2WO_6 (JCPDS No. 23-1074).[2]

We agree that EDS is a not a valid proof. However, we had observed the percentage of Gd (5%) as per the preparation at a particular location. The presence of the elements Gd, Zn, W and O in the catalyst is confirmed by XPS analysis. There are no XPS peaks for any other element. The statement may read as XPS confirms the purity of the catalyst, since there are no peaks for other elements. XPS peak of W confirms its presence in the material. Hence, the material reported is not a doubtful material.

References

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