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On the measured optical bandgap values of inorganic oxide semiconductors for solar fuels generation

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ABSTRACT

This article focuses on variation in the values for the optical bandgaps (E_g) experimentally reported for fourteen oxide semiconductors that have been studied for solar photoelectrochemical and photocatalytic environmental remediation applications. Both binary and ternary compounds have been included in this study. The variance in the reported values is much more severe for the ternary compounds relative to the binary counterparts. Factors related to semiconductor doping and size quantization have been carefully removed from playing a role in the presented data. Instead the variability is attributed to intrinsic errors associated with the extraction of E_g values from spectral data (for example, via Tauc plots), and to other sample-related factors such as surface functional groups and compound non-stoichiometry. Finally, suggestions for future, follow-up study are also given.

1. Introduction

The optical energy bandgap, E_g, is a fundamental property of the inorganic semiconductor in a photoelectrochemical (PEC) cell [1–3] for solar fuels generation. It dictates the amount of photon energy absorbed by the semiconductor from the excitation source (the Sun), and thence the ultimate photon-to-fuel conversion efficiency that can be achieved. During our ongoing, collaborative efforts to screen new generations of oxide semiconductor candidates for solar fuels generation [4–6], wide variations were noted in the reported bandgap values in the literature for a given semiconductor, especially for ternary oxides. It was of interest to examine whether these variations were universal in nature; this review article thus reports the results of such an examination.

First, we briefly outline the rationale for why the particular oxide semiconductor candidates (see Table 1 below) were chosen for this comparative study. Next, we summarize the methods that are commonly utilized for the E_g determination, so that the reader may glean an appreciation of the inherent assumptions and uncertainties involved in each approach. Finally, the review results are presented for fourteen oxide semiconductor candidates ranging from binary to ternary compounds. Importantly, the variations are *not* seen to be universal, and appear to be more severe for the ternary compounds than for their binary counterparts, although there are exceptions as elaborated below. Finally, this review will conclude with a discussion of possible causal factors in the variance of the reported E_g values.

2. Literature search methodology

Oxide semiconductors have a rich solid-state chemistry that makes them attractive for optimization in solar PEC and photocatalytic (PC) applications. In fact, the history of the PEC (and photocatalysis, c.f., Ref. [7]) community is rooted in oxide materials, and particularly in titanium (IV) oxide or TiO_2 [1,8,9]. The E_g value of this material (3.0–3.2 eV, see below, depending on the polymorph; see Table 1) is much too wide for effective utilization of the solar spectrum (as is the case for a few other candidates in Table 1). Nonetheless, this material is included as a candidate for this study for historical reasons and consequently the wealth of available data. Three other binary compounds (ZnO, WO_3, and Cu_2O) were included for comparison. Their choice simply reflects the intense scrutiny these materials have received, relative to other

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Table 1
Oxide semiconductor candidates included for this study.

Semiconductor	Structure type	Optical bandgap (E_g) range (eV)[a]	Comments
Binary			
TiO_2	Anatase	3.0–3.5	Value depends on polymorph, ~0.2 eV higher for the anatase phase than for rutile.
ZnO	Wurtzite	3.2–3.4	–
WO_3	Monoclinic	2.5–2.9	–
Cu_2O	Cuprite	2.0–2.2	Very negative conduction band edge.
Ternary			
$SrTiO_3$	Perovskite	3.2–3.8	Historically, one of the earliest ternary compounds studied for PEC applications.
$BiVO_4$	Scheelite	2.2–2.6	–
$Bi_2Ti_2O_7$	Pyrochlore	2.6–3.2	Other bismuth titanates also known; see Ref. [11].
$ZnFe_2O_4$	Spinel	1.7–4.8	–
$CuFe_2O_4$	Spinel	1.4–3.1	–
$PbMoO_4$	Wolfenite	1.7–4.1	–
$CuBi_2O_4$	Kusachite	1.4–1.8	–
$ZnNb_2O_6$	Columbite	3.6–4.1	–
$ZnWO_4$	Sanmartinite	3.1–4.4	–
$CuWO_4$	Wolframite	1.8–2.8	–

[a] Values rounded to two significant figures. More detailed analyses of variability appear in following tabulations.

binary compounds, for PEC solar fuels generation. Notably, and for example, iron oxide (Fe_2O_3) was omitted because of concerns associated with its bulk charge carrier transport deficiencies (i.e., it is a Mott solid with severe carrier trapping limitations) [10]. Finally, we underline that only experimental determinations of E_g are considered here. The uncertainties in E_g determination by band structure calculations (for example via density functional theory or DFT methods) still are severe enough to cloud other discussions related to variance in reported values such that it was deemed prudent to consider only experimentally-derived values for E_g.

The other ten compounds, selected for this study, were all ternary compounds (Table 1). These may be regarded as the "new-generation" oxides for PEC solar fuels generation. An exception is the perovskite compound: $SrTiO_3$ that has a long history of study [1,8], and was thus included for historical reasons. Compositionally, these ternaries may be regarded as solid solutions ("alloys") of the corresponding binary oxide components. For example, $ZnNb_2O_6$ is a 1:1 solid solution of ZnO and Nb_2O_5; less transparently, $BiVO_4$ is a 1:1 solid solution of Bi_2O_3 and V_2O_5.

In every case, the oxide was chosen such that a wide literature base was available for it affording robust statistics to be performed. The particular studies (and the E_g values reported therein) were chosen randomly so as to avoid bias in data selection; we will return to this important point later. The literature base selected for this review is also fairly recent, and the oxide materials under study were all polycrystalline and/or in thin film form. Single crystals, while relatively immune from structural defects, are hardly relevant to practical applications in a solar energy conversion sense where high surface area is paramount for efficient photon to chemical conversion. Nonetheless, they were included in isolated instances: for example, tables in Supplemental Information. These inclusion decisions were mainly prompted by the general paucity of bandgap data on metal tungstates in general.

Particular care was also paid to instances wherein effects such as size quantization [9] did not play a tangible role; thus data wherein such effects could have played a role were intentionally omitted for this study. Similarly, all the oxides discussed below were in their intrinsic electronic states and were *not intentionally* doped. Both size quantization as well as doping are known to significantly influence E_g values [8,9]; inclusion of such cases, obviously clouds the underlying objective of this study. Compound non-stoichiometry, however, does play a key role in the comparisons considered below and is an unavoidable consequence of the preparation and subsequent work-up (e.g., thermal anneal history) of these materials.

Finally, the oxide material selection in each case, reflected a broad spectrum of synthesis approaches such that generalizations could be made independent of this variable (see below). The E_g values, in all the cases presented below, also pertain to ambient temperature and pressure.

3. Bandgap determination by experiment

Inorganic semiconductors, unlike their organic counterparts, are characterized by a relatively small exciton (e^--h^+) binding energy such that a distinction between the optical bandgap and electronic (or "transport") bandgap, is redundant. On the other hand, the distinction between direct vs. indirect bandgaps is very relevant to the present discussion. If the valence band maximum and the conduction band minimum have the same crystal momentum (k-vector) in the Brillouin zone, then the resultant optical transition is termed a "direct" transition [12]. On the other hand, an indirect bandgap material would have to have phonon coupling for the optical transition to occur [12]. For example, the 1.1 eV bandgap in single-crystal Si is indirect. It is indeed possible, for a given material, to possess both direct and indirect optical bandgaps [see below]. We note here that the nature of the transition (direct/indirect) has important implications on the photon-to-chemical conversion efficiency in both the PEC and PC scenarios, via dictating charge carrier lifetime and thus the recombination rate.

Optical bandgaps are most directly measured on thin films or compact powder surfaces using UV–vis (or near-IR) spectrophotometric measurements. These measurements utilize the diffuse reflectance mode, although, in many instances, the sample is optically transparent such that transmittance measurements are also possible. The ultimate aim is to secure values for the absorbance or the absorption coefficient (α) as a function of wavelength. The reader is referred to an authoritative account of constraints on powder sample thickness and other measurement details in Ref. [13].

The Kubelka-Munk (K-M) radiative transfer model allows for calculation of reflectance (from the measured absorbance) from a layer that both scatters and absorbs light [12–14]. Within the

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