

Conference Paper

Identification and Detailed Characterization of Metal Oxide Powders As a Fundamental Chemical Product

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Abstract

Here we propose a method for identification and detailed characterization of metal-oxide powders with patterns of energy-resolved density of electron traps (ERDT) and conduction-band bottom (CBB) position, as a fingerprint, measured by newly developed reversed double-beam photoacoustic spectroscopy (RDB-PAS).

Keywords: Electron Traps, Photoacoustic Spectroscopy, Metal-oxide Powders, Degree of Coincidence

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1. Is It Possible to Identify Inorganic Powder Materials? — An Introduction

In the fields of chemistry and material science, "identification" is to specify a pure substance which is different from the others and, thereby, it is impossible to make scientific and/or technological discussion without identifying a substance. In the other words, "identification" is to describe the structure of a given substance using words, i.e., to put a unique name. This seems not so difficult, but whether it is possible to put name or not depends on whether it is possible to clarify the structure and, furthermore, it is necessary to determine what kind of structure should be described before the structural analyses. At present, nomenclature, putting name to substances, is made according to the rules [1–3] and guide [4] issued by International Union of Pure and Applied Chemistry (IUPAC). Organic and inorganic molecules as well as metal complexes are named based on their skeletons, arrangements of atoms bonded with each other, and they are uniquely named. Consequently, if their molecular formula are determined, they are named, i.e., identified. This identification as a molecule does make sense because they are predominantly used as solutions or gases but not as solids even if they are solid, i.e., for those identifications can be made for any materials in the phase of solid,

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liquid or gas. On the other hand, inorganic solids cannot be named as IUPAC stated in "Nomenclature of Inorganic Chemistry" [1] (p. 236a), as

This chapter deals with some aspects of terminology, nomenclature and notation for (inorganic) solids. However, in cases where detailed structural information is to be conveyed, fully systematic names can be difficult to construct.

Thus, surprisingly, IUPAC recommends us to give up identification of inorganic solid materials and we scientists have no concept of identification of solids so far.

2. Structural Information for Identification of Solids

Conversely, it may be possible to identify inorganic solids by finding appropriate parameters which describe their structure. The reasons why we think it difficult to find the appropriate parameters seem to be as follows:

(1) Both bulk and surface structures are necessary: Solids have surfaces and surface properties must not be the same even if bulk structure is the same. Furthermore, even if, this is not realistic, both bulk and surface structures are the same, powders of different size of bulk and/or surface must be different. Therefore, bulk/surface size should also be determined as one of required parameters.

(2) Macroscopic measurements are necessary: Among bulk and surface structures, surface structure of powders have been so far analyzed by microscopic methods such as electron microscopy or probe microscopy. There is no guarantee for that such microscopic results can be expanded to whole surface. Few macroscopic methods have been used for surface-structural analyses such as zeta-potential analysis or surface acidity-basicity analysis, though those methods cannot be comprehensive and general methods toward powders. It should be noted that specific surface area analysis, well-known popular analysis for powders, gives information of size of surface (or bulk) not reflecting the surface structure.

(3) Bulk is not always crystalline: It seems easy to determine the structure of bulk compared with that of surface, but that is limited to the cases of crystalline materials, which can be determined by powder X-ray diffractometry. Structural-analytical methods for non-crystalline or partly crystalline materials are negligibly found.

On the basis of these considerations, macroscopic analyses, if any, on, at least, (a) crystalline or no-crystalline bulk structure, (b) size of bulk/surface and (c) surface structure may be used for identification of inorganic powder materials. It is clear that

so far we have not yet found the method(s) satisfying the above-mentioned minimum three requirements.

3. Metal Oxides and Their Electron-trap Distribution

Wide variety of metal oxides are important fundamental chemical products manufactured and used in large scale in the world. As an attempt for identification of solid inorganic powder materials, metal oxides are chosen as a target in this study.

Almost all the metal oxides are categorized into semiconductor and/or insulator with electronic-energy structure composed of electron-filled valence band (VB), electron-vacant conduction band (CB) and bandgap separating VB and CB (**Fig. 1a**).

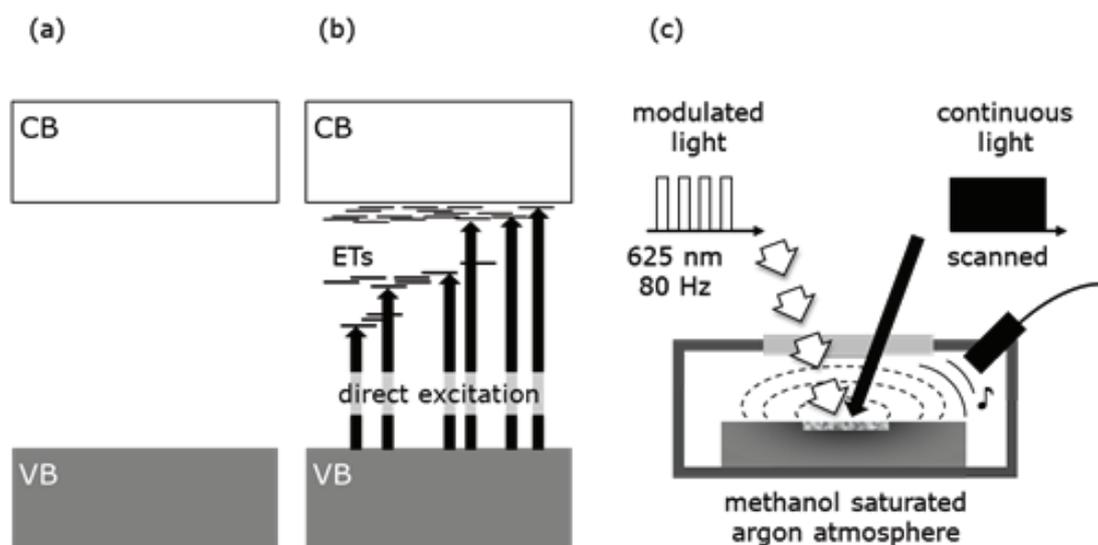


Figure 1: (a) Electronic structure and photoexcitation of semiconductors and insulators: band structure composed of conduction band (CB), valence band (VB) and band gap, (b) principle of RDB-PAS: filling of electrons by direct excitation of VB electrons to vacant ETs from deeper (lower in this figure) side to shallower (higher in this figure) side with light of wavelength scanned from longer side to shorter side and (c) schematic representation of an experimental setup of RDB-PAS.

Since, generally speaking, oxygen in metal oxides tends to be detached by heating in vacuum or under hydrogen atmosphere leaving electrons as a donor, all the metal oxides, except for few examples such as nickel oxide, exhibit n type-semiconductor property. Titanium(IV) oxide (titania) and tungsten(VI) oxide, known to be semiconductors, turn grey and blue, respectively, when heated under reductive atmosphere or irradiated in deaerated aqueous suspension in the presence of electron donors, which is attributed to the formation of titanium(III) and tungsten(V) ions, respectively. Such coloration is saturated even under the prolonged treatments suggesting that those metal oxides have electron-accepting levels originally before the treatments [5], i.e.,

they have "electron traps", which may be vacant donor levels liberated by transfer of electrons. Presence of such electron traps has been proposed in the 1970's [6] and reported to be mainly located on the surface [7], and therefore analysis of those electron traps may be related to the surface-structural analysis required for the identification.

It has been reported that deep-level transient spectroscopy (DLTS) can analyze energy-resolved density of electron traps (ERDT) of semiconducting solid materials, e.g., ERDT of titania thin films prepared by epitaxial growth was reported [8]. However, those reported analytical methods were limited to the measurement of deep (low energy) electron traps, not shallow traps located just below CB bottom (minimum) and no reports have been published for powder samples. A group of the present authors previously reported an ERDT-measurement method which could be applicable to powder samples through photochemical titration and two kinds of titania powder samples were used analyzed to obtain ERDT patterns [5]. The photochemical titration was performed toward UV-photoirradiated suspensions of titania powders in the presence of electron donors followed by reaction with methyl viologen under controlled pH conditions (In the first paper on similar titration with methyl viologen, the states storing electrons were assumed to be "titanium(III)" not electron traps [9]). In the pH titration, the standard electrode potential of methyl viologen/methyl viologen anion radical is constant irrespective of pH, while band structure including electron traps shifts depending on pH, and therefore ERDT can be obtained. However, the energy resolution was low due to difficulty in precise pH control during titration and the range of pH change was limited. Alternative methods, e.g., diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) [10] or a spectroelectrochemical method [11] also contain problems and hence not applicable to ERDT measurement of powder samples.

4. Development of Reversed Double-beam Photoacoustic Spectroscopy

In the above-mentioned photochemical titration [5] and DLTS [8], electrons in VB are photoexcited to CB and then trapped in electron traps to fill up all the electron traps, the energy of which is analyzed to obtain ERDT. On the other hand, in spectroelectrochemical method [11], electron traps are filled from the deeper (lower energy) side to shallower (higher energy) side by controlling the electrode potential. This seems better than the former methods, but it is necessary to prepare electrodes from powder.

Therefore, in ideal, ERDT should be measured for powder samples in their powder form by accumulating electrons in electron traps from deeper side to shallower side,

Inspired by the successful application of PAS to semiconducting metal-oxide powder samples reported by Toyoda [12-14], double-beam photoacoustic spectroscopy (DB-PAS) was developed for analysis of the photoinduced change of photocatalysts themselves under conditions similar to those in real applications of photocatalysis [15-17]. It was shown that continuous light does not have any effect on PA signal detection, and it was therefore possible to detect photoabsorption of a sample at the wavelength of continuous light irradiation in DB-PAS. One of the successful results of DB-PAS was for analysis of ET filling by bandgap excitation of titania photocatalysts; spectra of electron-filled ETs were obtained and total density of ETs in the titania samples were determined [17]. Then, in order to measure ERDT of metal-oxide powders, reversed double-beam photoacoustic spectroscopy (RDB-PAS) has been developed by modifying DB-PAS. In RDB-PAS, the mode of wavelength scanning is reversed; continuous light driving a photoreaction is wavelength-scanned (fixed wavelength in DB-PAS) and modulated (chopped) light generating the PA signal is wavelength-fixed (wavelength scanned in DB-PAS) [18]. The continuous light excite an electron in VB to electron traps along with capture of a simultaneously liberated positive hole by methanol and modulated light produce PA signal (sound at frequency of the modulation) for electrons captured in electron traps (**Fig. 1(b)(c)**). The practical analytical procedure has been reported elsewhere [19].

5. Representative ERDT Patterns of Titania Samples

Representative ERDT/CBB patterns for titania samples are shown in **Fig. 2**.

Figures in < > are total density of electron traps in the unit of $\mu\text{mol g}^{-1}$, and crystalline phases (A and a: anatase in major and minor components and R and r: rutile in major and minor components) and specific surface area in the unit of $\text{m}^2 \text{g}^{-1}$ are also shown. The CBB positions of anatase and rutile titanias were ca. 3.2 eV and 3.0 eV, respectively, which were in good agreement with the reported bandgaps (energy between CBB and VBT) [20]. Anatase-rutile mixture exhibited CBB between 3.0 and 3.2 eV. Thus, it seems that CBB positions (data) reflect bulk (crystalline) structure of samples. For the total density of electron traps, commercial titania powders showed almost proportional increase with their specific surface area irrespective of crystalline structure, anatase or rutile [18], suggesting that electron traps are predominantly located on the surface and that the total density reflects surface (or bulk) size of samples. Therefore

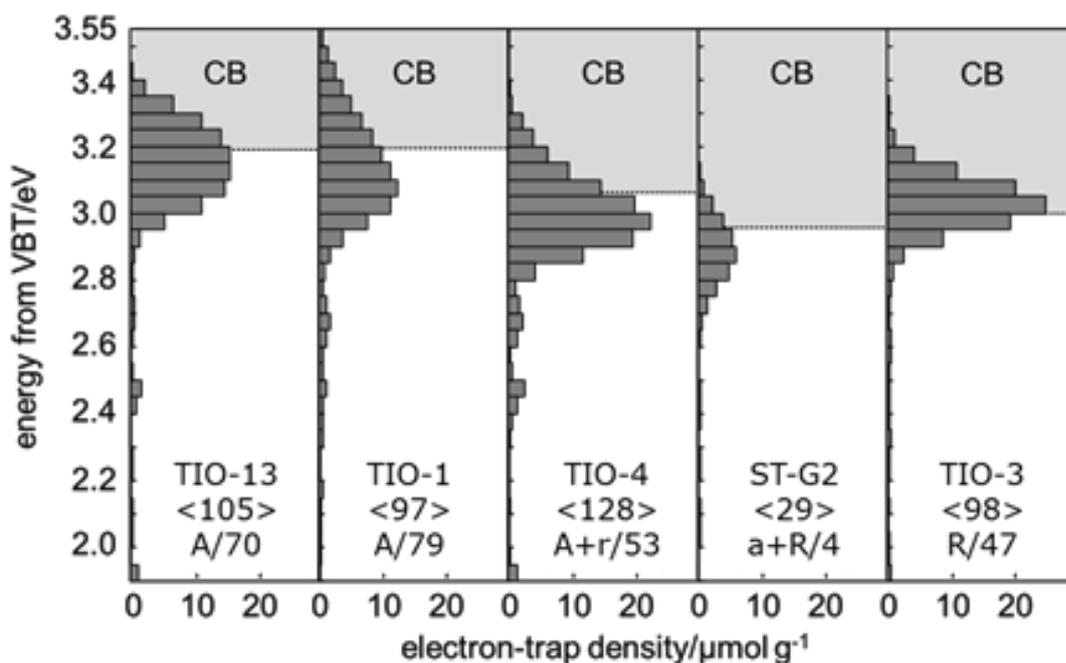


Figure 2: Representative ERDT/CBB patterns for titania powders. Figures in $\langle \rangle$ show total density of electron traps in the unit of $\mu\text{mol g}^{-1}$. Anatase and rutile are indicated by "A" ("a" in case of minor component) and "R" ("r" in case of minor component). Figures after / show specific surface area in the unit of $\text{m}^2 \text{g}^{-1}$.

information on bulk structure and surface/bulk size, which have been analyzed by, e.g., X-ray diffractometry and nitrogen-adsorption measurement, respectively, is including in ERDT/CBB patterns.

On the other hand, another information can be obtained in the patterns. For example, two anatase samples, TIO-1 and TIO-13 giving almost the same total density (and specific surface area) exhibited markedly different ERDT patterns. Since, as mentioned above, it seems that electron traps (at least of titanias) are located on the surface of particles, ERDT patterns may reflect surface structure, which have not been analyzed macroscopically, of samples. Although the correlation between actual surface structure and ERDT pattern is ambiguous at present, as far as the authors knowledge, RDB-PAS is only one method to obtain properties reflecting the surface structure of samples as a macroscopic method.

For all the samples in **Fig. 2**, electron traps appear at around CBB and a part of them have energy higher than CBB, i.e., electron traps were there above the bandgap. This seems a little strange from the standpoint of electronic states in the bulk. However, considering that photoabsorption coefficient for excitation of electrons in VB to electron traps is negligible (as no absorption is measured in photoabsorption spectroscopy), actual excitation to electron traps occurs from a high DOS (density of states) part below VBT and thus the energy of electron traps in ERDT patterns may be overestimated. This

is supported by the fact that ERDT patterns of two commercial titanias measured by photochemical titration method [5] were downward shifted compared with the patterns measured by RDB-PAS by ca. 0.1-0.2 eV [19]. Furthermore, electron traps, predominantly located on the surface of particles, are not obliged to have energy within bandgap as for electron traps in the bulk as in **Fig. 3**.

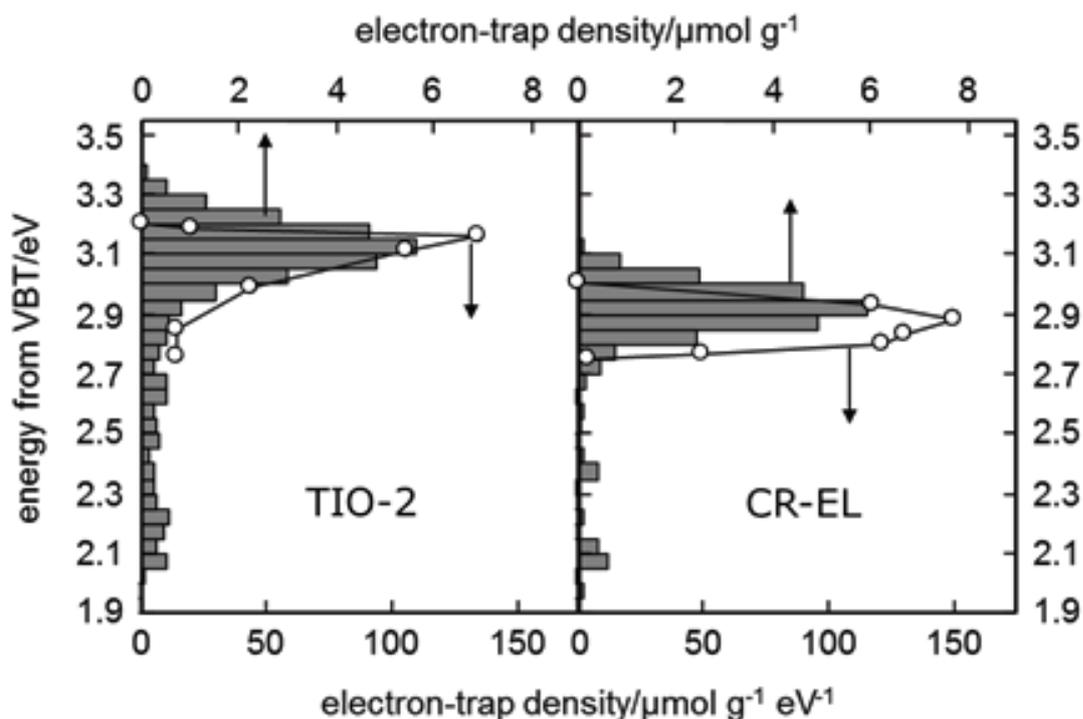


Figure 3: Comparison of ERDT patterns for JRC-TiO-2 and Ishihara Sangyo CR-EL measured by RDB-PAS (bars) and the photochemical titration method (open circles).

Anyway, even if such a problem in the estimation of absolute energy level of electron traps has not been solved, the above-mentioned results clearly show that ERDT/CBB patterns can be used as a fingerprint of titania powder samples. The other metal oxides such as tungsten(VI) oxide, cerium(IV) oxide and niobium(V) oxide similarly exhibited ERDT/CBB patterns. Only one exception the authors found is nickel oxide, presumably due the fact that nickel oxide is categorized into p-type semiconductor as an exception of n-type metal oxides.

6. Identification and Detailed Characterization of Metal Oxide Powders by RDB-PAS

Thus, it is suggested that ERDT/CBB patterns can be used as a fingerprint for identification of metal oxide powders as nuclear magnetic resonance (NMR) spectra have

been used for identification of organic compounds. Furthermore, it is expected that ERDT/CBB patterns are used for detailed structural analysis since they reflect structural characteristics of surfaces and RDB-PAS is, at present, only one possible method to analyze surface structure macroscopically.

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