

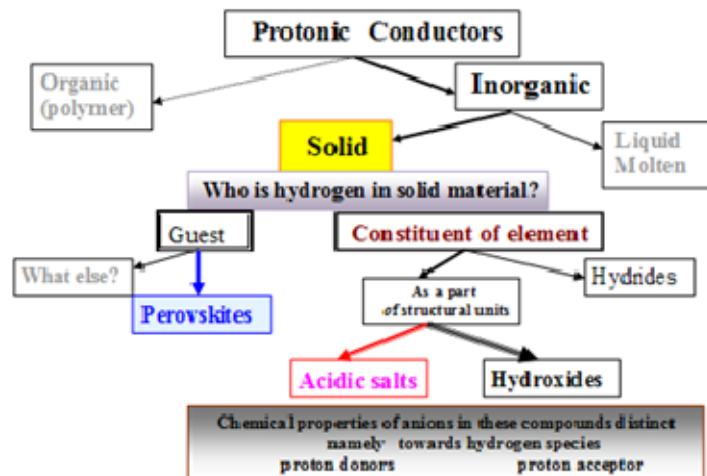
# VARIOUS TYPES OF HYDROGEN SPECIES STATE IN OXIDES FROM PHYSICAL, CHEMICAL OR JOINT VIEW POINTS: NORMAL OR EXOTIC

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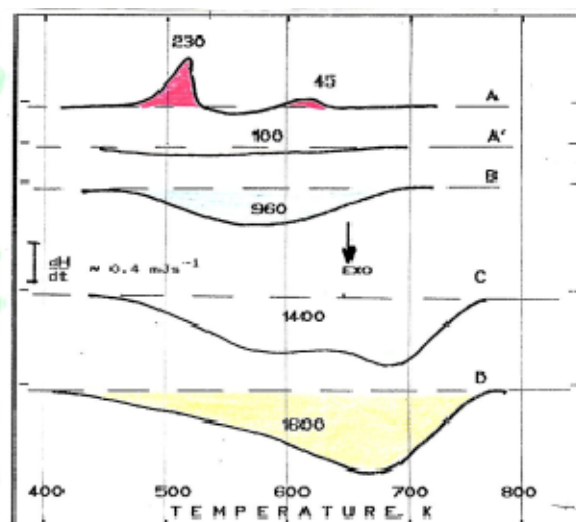
By using such title of this presentation author intends to highlight the specificity of the state of hydrogen species in inorganic materials as well as the question on so named “exotic state of hydrogen species in oxides”[1,2]. The matter is that the mutual relations “Hydrogen & Oxides” are interesting to different fundamental as well as applied directions of intellectual approaches to decide advanced aims of technologies including energetic one. However, if we limit ourselves to even only electrochemical energetic, it is necessary to distinguish two enough clear hydrogen species state: hydrogen is the “guest” and hydrogen is the “host”. As clear example, let us consider figure 1, where the main attention directed to solid inorganic ones.



**Figure 1.** Possible classification of protonic conductors taking into account the chemical state of hydrogen species.

The aim of this presentation is to follow faithfully the historical sequence of basic research and appearing of some definitions related to understanding the chemical state as well as the mechanism of migration in solids the hydrogen species. Nevertheless, let us start not from T. Grotthus (2006), but from Y.I. Frenkel (1926) and J.D. Bernal (1933). The matter is that the first has thought about only on liquid. Outstanding contributions of both last ones into developing of solid state science consist particularly into understanding the simultaneously effect of disordering in solid state (e.g. *Frenkel's defects*) and specificity of chemical bonds (e.g. *Bernal's grid of hydrogen bonds*). The direct joining of these conceptions to hydrogen behavior has been advanced by Bjerrum [3] proposed *various types of defects* of a grid of hydrogen bonds. Such approach to proton motion in solids has been joined in the middle of XX century with conception on superionic conductors, e.g. Ag-ion in

$\text{Ag}_4\text{RbJ}_5$ . However,  $\text{Ag}^+$  moves, supposedly, freely around bigger  $\text{J}^-$ -anions and the role of chemical bond could take into account only in next order approximation. Such simple model was accepted to consider the proton motion, at least in inorganic materials. Three families of them were perovskites, acidic salts and hydroxides, with proton bonded with oxygen ions. Factually, electron subsystems of acidic salts and hydroxides is considering as the passive "landing ground" for "running protons". Seemingly another situation is relating to hydrogen species in HTPC on the base of oxides. Firstly, the proton in HTPC is the "guest". But, secondly, this proton is very active "guest", which could effectively change the "life" of the "host": structural, physical and chemical properties. It was revealed not only for doped oxide, but also for nominally pure  $\text{BaCeO}_3$  prepared by skull technology. Using effect of isotopic exchange, it was shown [4] that even unlopped oxide contains hydrogen because of mixed valence of cerium ( $\text{Ce}^{+3}/\text{Ce}^{+4}$ ). At search the phase transition in pure material by DSC [5] it was revealed that the peak pair (curve A) can be obtained only after treatment at oxidizing conditions (dry oxygen). However at second run ( $\text{A}'$ ) effect was quite another. The treatment by water vapor (B), by dihydrogen (C) and by high vacuum (D) lead to enough strong and different by shape exo-effect effect. (Figure 2. Figure means the heat effect in J/mol).



**Figure 2.** Thermal properties of pure  $\text{BaCeO}_3$  after different treatment (see text).

Curves (on figure 2) B and C show, as example, that hydrogen as a "guest" changes cardinally the physic-chemical properties. Moreover, two peaks on C (near 580 K and 690 K) appears after molecular hydrogen influence. Probably, first peak reflects the result of previous proton intercalation by reaction of water molecule with oxygen vacancy like on the curve B. The second peak on C reflects the oxygen removal at reducing conditions like on the curve D. These data as well as many others from worldwide published ones give evidence of various physic-chemical states of hydrogen containing oxides. Usually it is relate to various states of hydrogen species. Although, not only macroscopic data but also most of spectroscopic ones should be explained sooner as various types of states of the threefold system "Oxygen ion- Electron-Proton". Of course, such statement is only trivial one and it

do not pretend to be new generalization. However, scientists are explaining usually experimental data using above mentioned components only in pairs. Such approach gives enough pleased results, particularly if it is concern to applied tasks. Therefore the term “normal state of hydrogen species” relates to more frequently studied system and any deviations from standard may be taken as “exotic” one.

Factually T. Norby [1] has advanced very intensively the idea on “exotic” state of hydrogen species in proton-conducting perovskites oxides. The impetus was done after revealing the “unusual” behavior of hydrogen at very strong reducing conditions: the open circuit potential of certainly arranged electrochemical cell . It has turned out that result could be considered as negatively charged ion carrier, i.d. hydride ion. The situation has been discussed last ten years, but unambiguously.

New step of the interest to hydride form in oxides was presented in [6-8]. (Only first name is indicated because of too much authors in each teams).The substitution of oxygen by hydride anions to form oxyhydrides has been difficult it requires highly reducing conditions without transferring an electron from the hydride. However, it was done even with BaTiO<sub>3</sub> whih is electronically conducting. To explain this was to advance the new idea on the role of d-electron orbital for this event.

It would like to note that specific interest to hydrogen species in oxides has arose not only after Iwahara’s (1981 year) discovery of *high-temperatures proton conductivity* (HTPC) in doped perovskites, but slightly later (1987 year), namely after the discovery of complex perovskites possess the superconducting properties. Really, YBa<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> (y≤7) hereafter (YBCO<sub>y</sub>) was synthesized in **February 1987** as *high-temperature superconducting oxide*. Investigations into the influence of hydrogen on the properties of YBCO<sub>y</sub> have already been started in *summer 1987*. The history and results of these investigations were described in many reviews in detail, e.g.[9,10]. What is common between HTSC and HTPC and Hydrogen?

In reality the synthesis HTSC and HTPC have been later and is now performed by similar variants of solid state chemical technologies. Moreover , the hydrogen **could** be used (for HTSC) or **must** be used (for HTPC) to control official duties (functions) of these compounds. Particularly, this generality is interesting to decide inclusive intellectual tasks from joint viewpoints of physics and chemistry.

The main objective of researches in the field of HTSC physics was to modify *the electronic subsystem of any oxides* using electrons of intercalated hydrogen atoms. Meantime, nuclei of hydrogen atoms (protons) were assigned the role of a probe sensitive to local features of magnetic fields in the lattice. Such explorations were carried out with a wide variety of physical methods at different laboratories in Europe, Israel, America, Japan, e.g. [11-16]. The results obtained in such direction were not universally unambiguous. Some effects, for example, the direction of variations in the lattice parameters or the T<sub>c</sub>- temperature upon hydrogen incorporation (see [9,10]) differed qualitatively. It has become evident that there are uncontrollable “*nonphysical*” factors, among which the process of hydrogen intercalation is of decisive importance.

At present, *chemical aspects* of the system “hydrogen – YBCO<sub>y</sub>” have been studied in sufficient detail taking into account the interaction between water vapor

[11-16]. One of these processes-deintercalation of oxygen- does not lead to hydrogen incorporation but accompanies two other processes-the formation of hydride-like “hydrogen bronze” at a low hydrogen content (less than 10 at. %) and the formation of a hydrogenated form in the initial cuprate matrix. The formula  $H_xYBa_2Cu_3O_y$  will be referred to as hydrocuprate at  $y < 7$  and as oxyhydrocuprate at  $y > 7$ ).

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