

SOLID STATE OXIDE IONIC CONDUCTORS

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The purpose of presented review is to summarize the results obtained in our laboratory during last twenty years at the investigation of oxide materials with fluorite-type structure as a sub-group of solid state ionics. The high temperature oxide materials, ZrO_2 , HfO_2 and ThO_2 -based materials, have been investigated from the point of view of chosen structural, electrical, mechanical and optical properties.

1. Introduction

"Solid state ionics" (or superionic conductors, fast ion conductors or solid electrolytes) is the term given to the substances which exhibit high ionic conductivities far below their melting temperatures. Many kinds of solid state ionics are known and they can be classified by various criteria [1]. In order to understand a mechanism of the diffusion of transport ions is appropriated to classify them by the structural aspects in combination with the kind of transport ions, such as Cu^+ , Ag^+ , Li^+ , Na^+ , K^+ and H^+ as cations and F^- , Cl^- and O^{2-} as anions [2].

The importance of oxide materials with the fluorite-type structure such as the stabilized (fully or partially) cubic zirconia, hafnia and ThO_2 -based solid solutions in many ceramic technologies is well known [3]. Both, ZrO_2 and HfO_2 , have three polymorphs, i.e. monoclinic, tetragonal and cubic phases. An addition of an appropriate amount of lower valent cations stabilizes (fully or partially) the cubic fluorite structure by substituting the sites for Zr^{4+} or Hf^{4+} ions, which avoids microcracking associated with the $t \rightarrow m$ transformation in ZrO_2 or HfO_2 . The introduction of such cations leads to the formation of oxygen vacancies in the oxygen ion sublattice to maintain the electrical charge neutrality. It results in a high oxygen ion conductivity. Y_2O_3 , CaO , MgO and several rare earth oxides R_2O_3 ($R = Sc, Yb, Tb, Gd, Er$, etc.) are used as stabilizers. Thoria has the cubic fluorite structure up to the melting point and shows a higher oxygen ion conductivity with addition of Y_2O_3 , La_2O_3 and Nd_2O_3 [4].

In spite of the technological importance of solid state ionics, many mechanisms and properties are not fully clarified. In order to obtain an unified principle of superionic

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behaviour further experimental as well as theoretical studies on various solid state ionics are necessary. The object of the present paper is to review our contribution to this principle from the point of view of experimental study of the high temperature oxide materials and the results obtained during last twenty years.

2. Yttria, most used stabilizer of structure

Yttria (Y_2O_3) is one from the most common stabilizers used to improve the properties in the case of ZrO_2 and HfO_2 . Its structure is described as a modified fluorite-type cubic structure with one fourth of the anion sites vacant and regularly arranged [5].

The undoped Y_2O_3 is a mixed, p - type and ionic conductor at high oxygen partial pressure and intermediate temperatures [6, 7]. The ionic contribution to the conductivity becomes significant at temperatures $> 700^\circ C$ and $PO_2 < 10^{-7}$ MPa [8]. The significant softening of Y_2O_3 at temperatures $> 700^\circ C$ corresponds to the increased participation of interstitial oxygen ions in the deformation process. The structural data, temperature dependence of electrical conductivity and microhardness, the influence of oxygen partial pressure indicate the important role of oxygen interstitials in the defect structure of undoped Y_2O_3 at high temperatures and high oxygen partial pressures [8].

The study of mechanical properties revealed four deformation mechanisms at room temperature [9]: 1) generation and motion of the point defects (most probably the interstitial oxygen), 2) generation and the motion of dislocations, 3) cracking and 4) formation of bands having the reoriented lattice; this mechanism is observed quite rarely at room temperature, the cracks are formed usually instead of the bands.

3. Fully - and partially - stabilized zirconia

The fully - stabilized zirconia is a good oxygen ionic conductor which can be used for various technical applications. This material shows predominantly ionic conductivity in a wide range of oxygen partial pressures when the cubic phase is fully - stabilized with an alkaline earth or a rare earth element. The dominant structural defects under ambient conditions (air, low temperatures) are oxygen vacancies. Besides some studies using CaO as a stabilizer [10 - 12], we have used mainly Y_2O_3 as a stabilizer to form yttria - stabilized zirconia (YSZ). In spite of technological importance, the studies of the physical properties in ternary systems of the stabilized ZrO_2 doped with small additions of the transition metal oxides are not fully known [13]. These impurities may effect various physical and chemical properties of zirconia. Therefore, our main attention was paid to these systems, where the fully - stabilized ZrO_2 is doped with WO_3 , Co_2O_3 , Cr_2O_3 and Fe_2O_3 in both structural forms, i.e., single crystals as well as polycrystalline ceramics [14 - 23].

Materials with a high ionic conductivity as well as a high thermal shock resistance are required for many applications, e.g. the oxygen sensor in metallurgy [24]. The addition of suitable impurities is a way to improve both the ionic conductivity and the thermal properties of stabilized ZrO_2 .

The kind of incorporation of tungsten ions into the YSZ lattice is a function of their concentration. The W^{6+} ions enter the interstitial positions at 0.1 wt.% WO_3 . Both the interstitial and the substitutional sites are occupied by W^{6+} ions in the structure at the higher dopant concentrations. This structural model of solid solution is in a good agreement with the measured physical properties. The dependence of lattice parameter, defect concentration, microhardness and optical absorption on the impurity concentration indicates an anomalous course at 0.1 wt.% WO_3 [4]. The conductivity mechanism in the bulk for both forms (single crystal and polycrystalline ceramics) is identical (i.e. hopping of oxygen vacancies). The observed decrease of intensities in the defect - induced Raman bands is due to the strong electronic influence of W^{6+} cations on their environment and the decrease of the number of oxygen vacancies in the structure.

The microhardness is independent on the tungsten concentration above $375^\circ C$, because the tungsten containing impurity phases are absent at these temperatures [19, 22]. Comparing the thermal diffusivity of both samples, YSZ and YSZ + 1 wt.% WO_3 , it can be seen that the sample containing WO_3 has a higher value of thermal diffusivity. It is assumed that this fact is caused by a higher phonon velocity. The difference in the specific heat for both samples is higher than would follow from the difference in the composition. This fact is due to the change in the grain boundary surface, i.e. due to the surface of non-equilibrium phase [16].

The similar structural model as was found to be valid for YSZ doped with WO_3 , is valid also in the case of YSZ doped with cobalt oxide (Co_2O_3), i.e. the formation of two types of solid solutions. Moreover, a part of cobalt ions is reduced from the valence state (III) to (II). The concentration and structural changes influence the properties of the oxygen sublattice resulting in an observed conductivity maximum in dependence on the cobalt concentration in the samples. The influence of cobalt doping on the microhardness and optical spectra is similar as in the case of tungsten and chromium presence in YSZ [15, 23, 25].

YSZ and Cr_2O_3 -doped YSZ are found to be purely ionic conductors in the temperature range $300^\circ C - 1000^\circ C$ in air. The conductivity does not follow a simple Arrhenius - type temperature dependence, but has a temperature dependent activation energy assigned to the ordering and the association of oxygen vacancies [21, 26]. This fact reflects itself also in the IR line width of Reststrahlen peak at 470 cm^{-1} and in the reducing of disorder of oxygen sublattice in the defect - induced Raman spectra. The same fact is supposed to have a responsibility also for the step-like character of temperature dependence of microhardness [18].

The partially - stabilized zirconia (PSZ) shows excellent mechanical properties and a good oxygen conductivity. These properties can be well used in the ceramic oxygen sensor production, where a good thermal shock resistance combined with a good ionic conductivity are important [27, 28]. The concentration of the MgO stabilizer in the MgO -PSZ system influences the phase composition (the ratio between cubic and monoclinic phases) and consequently the microstructure and electrical conductivity. The increase of MgO concentrations results in the decrease of m- ZrO_2 volume portion in favour of the cubic phase and thereby in the increase of oxygen vacancy number and

electrical conductivity. The average grain size decreases with the increasing amount of stabilizer and the thickness of intergranular layers is dependent on the MgO concentration too [29, 30].

When yttria-stabilized zirconia (YSZ) is exposed either to reducing atmospheres (e.g. vacuum) or to the electrical currents [31, 32], it becomes coloured. The influence of annealing in vacuum on ZrO_2 and ZrO_2 -based solid solutions depends on the temperature, the oxygen partial pressure, the annealing time and on the cooling rate after annealing. The high temperature annealing (i.e. $T > 1400^\circ C$) in a reducing environment followed by quenching causes the black colouring of crystal [33]. The annealing of YSZ in vacuum causes the increase of number of electrons. The reduction processes of crystal at annealing in vacuum depend also on the composition of solid solution, i.e. on the type and concentration of stabilizing oxide. The increase in concentration of excess of electrons gives evidence for the mixed ionic-electronic character of electrical conductivity. The observed differences in the conductivity values of sample, the colour of which is changing from the light-green up to the black one, can be evidently ascribed to the disordering in the oxygen sublattice due to the different degrees of reduction and consequently due to the different concentrations of oxygen vacancies and excess of electrons [34].

The opinion about the darkening of fully - and partially - stabilized zirconia is not unique as evidenced by the literature [35, 36]. According to our investigation, the stoichiometry changes and the related lattice defects (colour centers) seem to be the main reason of darkening of crystal.

4. Hafnia - stabilized with rare earth oxides

HfO_2 was selected as a promising material for solid electrolytes at low oxygen potentials [37]. Its cubic fluorite - type structure must be stabilized in the same way as in the case of ZrO_2 . The more complex view on the structure and properties of the HfO_2 -based systems, stabilized with the rare earth oxides R_2O_3 ($R = Sc, Yb, Y, Tb, Gd, Er$) were obtained by the investigation of the structure, the infrared reflectivity and the Raman scattering as well as the electrical conductivity of these systems in the single crystalline form [38, 39]: 1) $HfO_2 - R_2O_3$ ($R = Sc, Yb, Y, Tb, Gd, Er$) are the substitutional cubic solid solutions, 2) single crystals $Sc_{0.26}Hf_{0.74}O_{1.87}$ show a stable rhombohedral substitutional arrangement, 3) the observed IR-active phonons and defect-induced Raman spectra are related to the structure differences between 85 mol% $HfO_2 + 15$ mol% R_2O_3 ($R = Yb, Y, Tb, Gd, Er$) (O_2^+) and 85 mol% $HfO_2 + 15$ mol% Sc_2O_3 (D_3^+). 4) Krönig analysis gave the resonant frequencies of transversal and longitudinal modes, ω_{TO} and ω_{LO} and 5) for all dopants investigated the electrical conductivity decreases as the dopant radius increases. The activation energy for conduction was found to increase with the dopant ionic radius. The fact that the highest electrical conductivity was obtained with $HfO_2 + Sc_2O_3$ system suggests that the deformation of coordination polyhedron around cations and the radius ratio r_d/r_n (r_d - dopant radius, r_n - host cation radius) play an important role in the determination of electrical conductivity behaviour.

5. Thoria - based systems

The study of arbitrary system requires, in general, a good knowledge about the structural properties of solid solutions in the investigated systems.

ThO_2 and its solid solutions have the fluorite - type structure over the whole temperature range and from this point of view, like CeO_2 , is a more suitable material for basic research, in comparison with ZrO_2 - or HfO_2 -based systems [4]. Thoria - based polycrystalline ceramics have an exceptionally high melting point ($3300^\circ C$). Materials on the basis of ThO_2 have conductivities one to two orders of magnitude lower than ZrO_2 solid solutions. Their practical applications are restricted to the low oxygen partial pressure, PO_2 , since at the higher oxygen partial pressures, p - type electronic conductivity prevails.

The formation of solid solutions investigated by X - ray diffraction methods and density measurements in the systems $xCaO - (1-x)ThO_2$ and $xYO_{1.5} - (1-x)ThO_2$ over the broad composition range, $0 < x \leq 0.40$, has shown a one-phase fluorite - type cubic solid solution $Ca_xTh_{1-x}O_{2-x}$ in the system $CaO - ThO_2$. It contains substitutional as well as interstitial cations. In the system $YO_{1.5} - ThO_2$, there exists a one - phase fluorite - type cubic solid solution $Y_xTh_{1-x}O_{2-x/2}$ in the range $0 < x \leq 0.03$. At higher concentrations ($x \geq 0.04$), the solid solutions decompose into two cubic fluorite - type solid solutions. They differ in the distribution of Y^{3+} ions between the substitutional and interstitial positions and in the vacancy concentration [40].

The properties of CaO - doped ThO_2 have been studied [11, 41, 42], but more attention has been paid to the trivalent ion - doped ThO_2 systems, due to a higher electrical conductivity [11, 43, 44]. The undoped thoria has a mixed electrical conductivity, ionic and electronic. The ionic conductivity is predominant at high temperatures and intermediate oxygen partial pressures. It probably arises from the defects generated in the presence of heterovalent impurities. The p - type conductivity of undoped thoria is due to the nonstoichiometry arising at high oxygen partial pressure (model of H centers) and is proportional to the oxygen partial pressure raised to the $1/4^{th}$ power [43].

ThO_2 - based solid solutions which contain rare earth metal oxides, R_2O_3 ($R = La, Nd$), were found to be predominantly ionic conductors at intermediate oxygen partial pressures. With increasing concentration of trivalent cations, the region of ionic conductivity is shifted in the direction of higher PO_2 . The contribution of p - type conductivity at high oxygen partial pressures is proportional to $PO_2^{1/4}$ (model of H centers) [43].

Under special technological conditions, it is possible to prepare transparent ceramics (i.e. nearly theoretical density). The transparent ceramics are characterized by low porosity, homogeneous microstructure and absence of microcracks, second phases and segregations on the grain boundaries. Transparent $ZrO_2 - Y_2O_3$ ceramics were obtained by the low temperature sintering of ultrafine powders by the hydrolysis technique [45]. Transparent $ThO_2 - Y_2O_3$ can be prepared by an oxalate method [46]. The transparent thoria - yttria ceramics proved to be the one - phase structure of the fluorite - type with a high electrical conductivity and a good stability in liquid sodium [46, 47].

6. Proton conducting solids at high temperatures

High temperature proton conducting solids are useful materials. However, many protonic conductors decompose at temperatures above 3000°C [48]. About ten years ago, it was found that certain perovskite - type oxide solid solutions, e.g. BaCeO₃, SrCeO₃, which are ionic or electronic conductors, exhibit the protonic conduction in an atmosphere containing hydrogen or steam at high temperatures [48].

The dissolved hydrogen is primarily present as substitutional hydroxide groups, (OH)_o. These defects may equivalently and more simply, be treated as interstitial protons H_i, which can be compensated by negative defects like electrons, oxygen interstitials, or acceptor dopants.

The perovskites based on SrCeO₃ or BaCeO₃ in which lower valence cations are partially substituted for cerium have the general formula SrCe_{1-x}M_xO_{3-α} or BaCe_{1-x}M_xO_{3-α}, where M is a rare earth element, x is approximately 0.10 and α is the number of oxygen vacancies per the perovskite - type unit cell. These oxides exhibit protonic conduction under a hydrogen-containing atmosphere at high temperature. Doping by divalent cations is essential for the appearance of protonic conduction in these oxides. BaCe_{1-x}Ca_xO_{3-α}, where x = 0, 0.02, 0.05, 0.10 and 0.15 [49] is an example of this type of conductor.

7. Applications

The high temperature applications of zirconia are related to its electrical properties, namely its ionic and electronic conductivities and thermoelectronic emission. Such applications often occur in the energy technology. In the energy production, zirconia is useful in three applications: (1) in heating elements for the furnaces working in oxidizing atmospheres in the range of 1500° - 2000°C, (2) as a cathode material for an air plasma source and (3) as an electrode material for the conversion of energy by the open-cycle magnetohydrodynamic (MHD) devices. For the conservation of energy, zirconia is useful as an oxygen sensor for monitoring the oxygen content in combustion chambers or in the steelmaking. In the energy storage applications, zirconia electrodes are used in high temperature thermolysis of water to produce the hydrogen [1].

The partially-stabilized zirconias (PSZs) have received attention as the tough structural ceramics. This interest stems largely from the transformation toughening behaviour of PSZs. Such toughened ceramics include the metastable precipitates of tetragonal zirconia in a matrix of the cubic (c) phase. The martensitic transformation from tetragonal (t) to monoclinic (m) zirconia, which is accompanied by a volume increase of almost 5% makes an important contribution to its toughness. Zirconia alloys which exhibit this type of toughening are referred to as transformation toughened zirconia (TTZ) [27].

Stabilized HfO₂ has several advantages over stabilized ZrO₂ because of superior physical properties. Hafnia fully-stabilized by additions of alkaline earth or rare earth oxides presents many possibilities for the exploitation because of its refractory, electrolytic, neutron-absorption and chemical inertness characteristics. It has been recommended for use in the solid electrolyte oxygen sensors in the molten metals and for use

as the high-temperature electrodes and low-temperature current leadouts for (MHD) generators. However, the uses and studies of stabilized hafnia are limited because of the high cost [37].

Among the oxide electrolytes, thorium-based materials are important for the applications in high-temperature galvanic cells, fuel cells, oxygen pumps and sensors. However, the use of ThO₂ is restricted because of being a nuclear fuel material. Therefore, the development of solid electrolytes functional at the low oxygen potentials instead of ThO₂-based electrolytes is required [1].

Proton-conducting solid electrolytes are of great interest due to their potential applications as the membranes in many more electrochemical devices, e.g. advanced fuel cells, H₂ sensors, steam electrolyzers for H₂ production and electrochromic optical displays [48].

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