Structural transformations, water incorporation and transport properties of tin-substituted barium indate

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ABSTRACT

Incorporation of water into tin-substituted $BaIn_{1-x}Sn_xO_{3-\delta}$ (x = 0.1–0.3) is shown to influence crystal structure at room temperature, structural transformations at high temperatures and ionic transport properties of the materials. Increasing tin content stabilizes oxygen vacancy-disordered perovskite-type phase, which together with large changes of the unit cell volume occurring during hydration and dehydration processes, result in a complex structural behavior, as documented by high-temperature X-ray diffraction and thermogravimetric studies. Impedance spectroscopy measurements at elevated temperatures (350–800 °C) revealed very high proton conductivity in $BaIn_{.8}Sn_{.2}O_{3-\delta}$, exceeding $1.1 \cdot 10^{-3}$ S cm^{-1} at 500 °C, with high values of the transference number in wet air. At the same time, relaxation kinetics of the electrical conductivity showed a monotonous nature, which indicates negligible component of the electronic hole conductivity in the hydrated material. The oxides are extremely moisture-sensitive, which results in a significant mechanical stability problems, affecting possibility to prepare electrolyte membranes.

1. Introduction

Conventionally, Solid Oxide Fuel Cells (SOFC) are built using oxygen ion-conducting electrolyte, but in recent years a new concept of implementation of proton-conducting electrolyte has been proposed. Such approach provides major benefits, including possibility of lowering of cell's operation temperature, better fuel utilization, as well as elimination of some of materials-related issues [1]. This is related to a fact that values of proton conductivity in the best so far developed solid oxide electrolytes at relatively low temperatures of 500–700 °C are comparable to that of oxide ion conductivity at much higher temperatures of 800–1000 °C [2–4].

Since the pioneering research conducted by Iwahara et al. [5], there have been numerous reports published concerning proton-conducting acceptor-doped perovskite-type oxides [6–8], denoted usually as $AB_{1-x}M_xO_{3-\delta}$ (typically, A: Ba, Sr; B: Zr, Ce, In, Sn; M: different +3/+2 elements). If synthesized in dry, hydrogen-free atmosphere, such materials do not contain protons, but easily react with water (or hydrogen) at elevated temperatures, becoming proton conductors [9]. Favored mechanism of proton incorporation is given by the reaction: $H_2O + O_O^x + V_O^{\bullet\bullet} \leftrightarrow 2OH_O^{\bullet}$ [10,11]. Research on isotope effect in perovskite-type proton conductors revealed that transport of protons through crystal lattice is due to the Grotthuss mechanism [12], which consists of a rotational diffusion of proton around oxygen anion and hopping to the neighboring oxygen ion.

It is known that high values of ionic conductivity of O^{2-} in perovskite-structured materials are connected to disordering of oxygen vacancies, which improves mobility. Such materials, especially having cubic symmetry, show remarkably high oxygen ion conductivity, and are considered as candidate solid electrolytes, for example for application in SOFCs [13–16]. While large increase of a concentration of $V_O^{\bullet\bullet}$ by acceptor doping on A- or B-site of the perovskite-type oxide can improve material's conductivity, for high values of the oxygen non-stoichiometry (e.g. $\delta \approx 0.5$) long-range ordering of the anion sublattice may occur, affecting ionic transport considerably [1,17]. Large values of the oxygen nonstoichiometry may favor high proton concentration, as the theoretical amount of the incorporated water cannot exceed the value of δ in the dry state. Interestingly, isotropic (cubic) structure also favors hydrogen migration in the lattice [18–20], while any distortions from the ideal structure may lead to an increase of the activation energy of proton conductivity [21].

In 2004 Norby et.al. [22] noted that there exists a correlation between a difference of A and B cations electronegativity and enthalpy of the hydration reaction. Namely, higher electronegativity difference limits amount of protons incorporated into the crystal structure and lowers proton conductivity. Concerning activation energy of a jump of

Table 1
Refined structural parameters of studied $BaIn_{1-x}Sn_xO_{3-\delta}$ at RT.

Assumed composition in dried state	Preparation conditions (see text for details)	Phase composition	Unit cell parameters [Å]	Normalized unit cell volume V [Å³]
$BaIn_{0.9}Sn_{0.1}O_{2.55}$ (BIS1)	stored	$Ibm2$ (59 wt.%)	$a = 6.0285(5)$ $b = 16.8486(17)$ $c = 5.9626(5)$	75.70(1)
		$P4/mmm$ (41 wt.%)	$a = 4.1914(3)$ $c = 8.8484(10)$ $c/2a = 1.056$	77.72(1)
	dried	$Ibm2$	$a = 6.0286(3)$ $b = 16.8406(9)$ $c = 5.9672(3)$	75.73(1)
	hydrated	$P4/mmm$	$a = 4.1907(2)$ $c = 8.8868(6)$ $c/2a = 1.060$	78.03(1)
$BaIn_{0.8}Sn_{0.2}O_{2.60}$ (BIS2)	stored	$Pm-3m$ (36 wt.%)	$a = 4.2159(1)$	74.94(1)
		$P4/mmm$ (64 wt.%)	$a = 4.2120(3)$ $c = 8.4876(16)$ $c/2a = 1.008$	75.29(1)
	dried	$Pm-3m$ (28 wt.%)	$a = 4.2180(1)$	75.04(1)
		$P4/mmm$ (72 wt.%)	$a = 4.2069(3)$ $c = 8.4754(16)$ $c/2a = 1.007$	75.01(1)
	hydrated	$P4/mmm$	$a = 4.1880(2)$ $c = 8.8036(5)$ $c/2a = 1.051$	77.20(1)
$BaIn_{0.7}Sn_{0.3}O_{2.65}$ (BIS3)	stored	$Pm-3m$	$a = 4.2146(1)$	74.86(1)
	dried	$Pm-3m$	$a = 4.2369(1)$	76.06(1)
	hydrated	$Pm-3m$	$a = 4.2407(1)$	76.27(1)
	dried (rapidly cooled)	$Pm-3m$	$a = 4.2034(1)$	74.269(3)
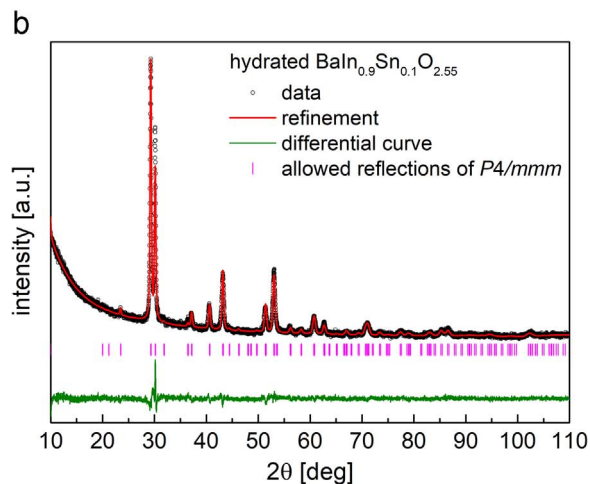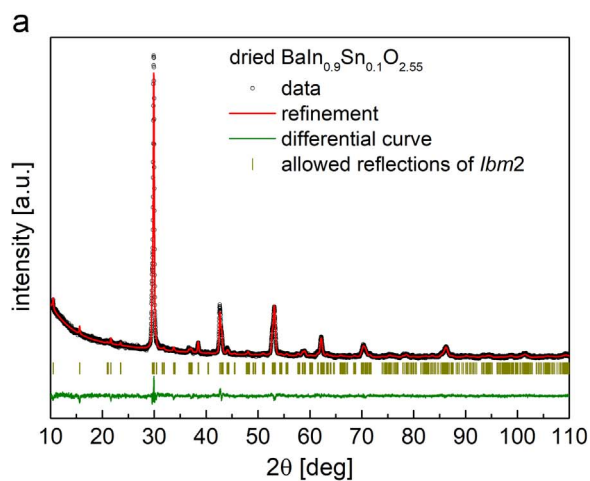
Fig. 1. Diffractogram with Rietveld analysis for a) dried and b) hydrated BIS1. Data recorded at RT.
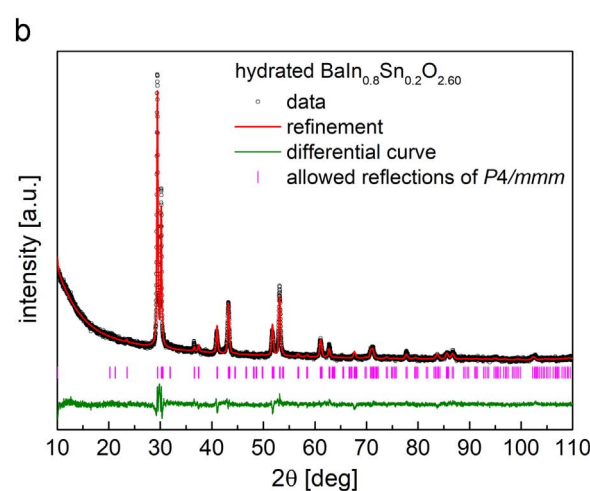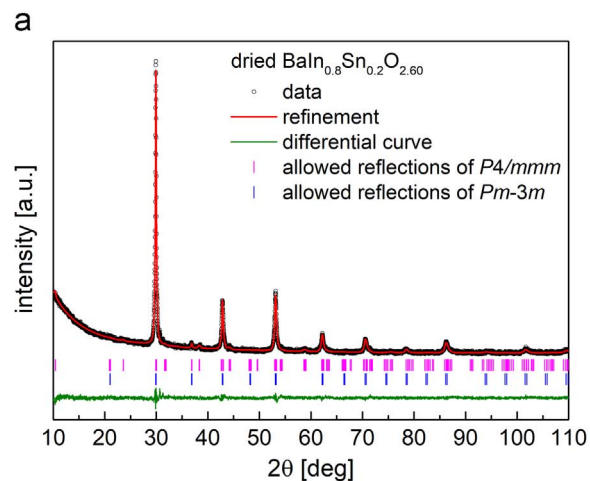
Fig. 2. Diffractogram with Rietveld analysis for a) dried and b) hydrated BIS2. Data recorded at RT.