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Investigations on the thermo-chemical stability and electrical conductivity of K-doped $Ba_{3-x}K_xCaNb_2O_{9-\delta}$ (x = 0.5, 0.75, 1, 1.25)

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ABSTRACT

In this paper, we report the synthesis, crystal structure and electrical transport properties of new K-doped $Ba_3CaNb_2O_9$ (BCN) and investigate their chemical stability in H_2O and pure CO_2 at elevated temperature. The powder X-ray diffraction (PXRD) of $Ba_{2.5}K_{0.5}CaNb_2O_{9-\delta}$, $Ba_{2.25}K_{0.75}CaNb_2O_{9-\delta}$, $Ba_2KCaNb_2O_{9-\delta}$, and $Ba_{1.75}K_{1.25}CaNb_2O_{9-\delta}$ showed the formation of a single-phase double perovskite ($A_3BB'_2O_9$)-like cell with a lattice constant of $a \sim 2a_p$ (where a_p is a simple perovskite cell of ~4 Å). Perovskite-like structure was found to be retained after treating with CO_2 at 700 °C and also after boiling H_2O for 120 h. The lattice constant of CO_2 and H_2O treated samples was found to be comparable to that of the corresponding as-prepared compound. The total electrical conductivity of all the investigated K-doped BCN increases with increasing K content in BCN in various atmospheres, including air, dry H_2, wet N_2 and wet H_2. The electrical conductivity in dry and wet H_2 atmospheres was found to be higher than that of air in the temperature range of 300–700 °C, while in wet N_2 a slightly lower value was observed. Among the compounds investigated in the present study $Ba_{1.75}K_{1.25}CaNb_2O_{9-\delta}$ showed the highest total electrical conductivity of 1×10^{-3} S/cm in dry H_2 at 700 °C with an activation energy of 1.28 eV in the temperature range of 300–700 °C.

1. Introduction

Solid-state (ceramic) and organic polymer based proton conductors find potential technological applications in numerous solid-state ionic devices (SSIDs) that include proton exchange membrane fuel cells (PEMFCs), catalysis, chemical synthesis, H_2 pumps, and gas sensors. To date, commercial PEMFCs are primarily based on a proton conducting organic sulfonated tetrafluoroethylene based fluoropolymer, well-known as a Nafion, electrolyte and Pt–C electrodes [1–5]. Attempts have been made to develop highly efficient, durable and economically viable proton conducting fuel cells (PCFCs) using ceramic proton conductors [1–5]. To this end, the ABO_3 perovskite-type structured Y_2O_3-doped $BaCeO_3$ (BCY) is being considered as a membrane for PCFCs, which exhibits good proton conductivity in wet H_2 at elevated temperatures. However, there are several problems with BCY due to its poor chemical stability in CO_2 containing atmospheres and in high levels of humidity [6–10]. Attempts had been made to improve the chemical stability and to maintain high proton conductivity simultaneously. Partial replacement of Ce by Zr in BCY was found to improve the chemical stability in CO_2, but the electrical (proton) conductivity decreases with the increasing Zr content [11].

The Nowick group [12] has investigated the proton conductivity of several double perovskite-related $A_3BB'_2O_9$-type structured $Ba_3Ca_{1+x}Nb_{2-x}O_{9-\delta}$ (BCN) and were found to be chemically stable against reaction with CO_2 over a wide range of temperature. Our recent work also showed that the partial substitution of Ta for Nb on the B-site in BCN exhibited a long-term chemical stability in CO_2 at 800 °C and in boiling H_2O for 168 h [13]. Ta-doped BCN showed a proton conductivity of 5×10^{-4} S/cm at 400 °C in wet N_2 or H_2. However, the BCN based ceramics showed a very large grain-boundary and electrode contributions to the total conductivity which limit their application in PCFCs [13].

The present approach involves partial replacement of Ba by K on the A-site in the double perovskite-type structure BCN to make dense materials and decrease the large grain-boundary contributions to the total electrical conductivity. We doped with K due to its similar ionic radius to that of Ba in the perovskite structure [14] and also to increase the basicity of the perovskite, which appears to be a crucial factor affecting the H_2O uptake capacity of the material and in-turn affects the protonic conductivity. At 700 °C, potassium oxide forms a hydroxide at a low equilibrium partial pressure of water (pH_2O) of about 3×10^{-7} atm, while six orders of magnitude higher pH_2O is required for the formation of $Ba(OH)_2$ from BaO under the same conditions [4,15]. Accordingly, an alkali oxide should be an effective dopant due to its very high basicity. Virkar and his coworkers reported a proton conductivity of ~4×10^{-3} S/cm in wet air at 700 °C for K-doped $BaZrO_3$ [16]. To best of our knowledge, there have been no studies on K-doped BCN reported to date. We report, for the first time, the effect of K substitution for Ba in BCN on electrical conductivity in various atmospheres, including air, dry and humidified atmospheres as a function of temperature.

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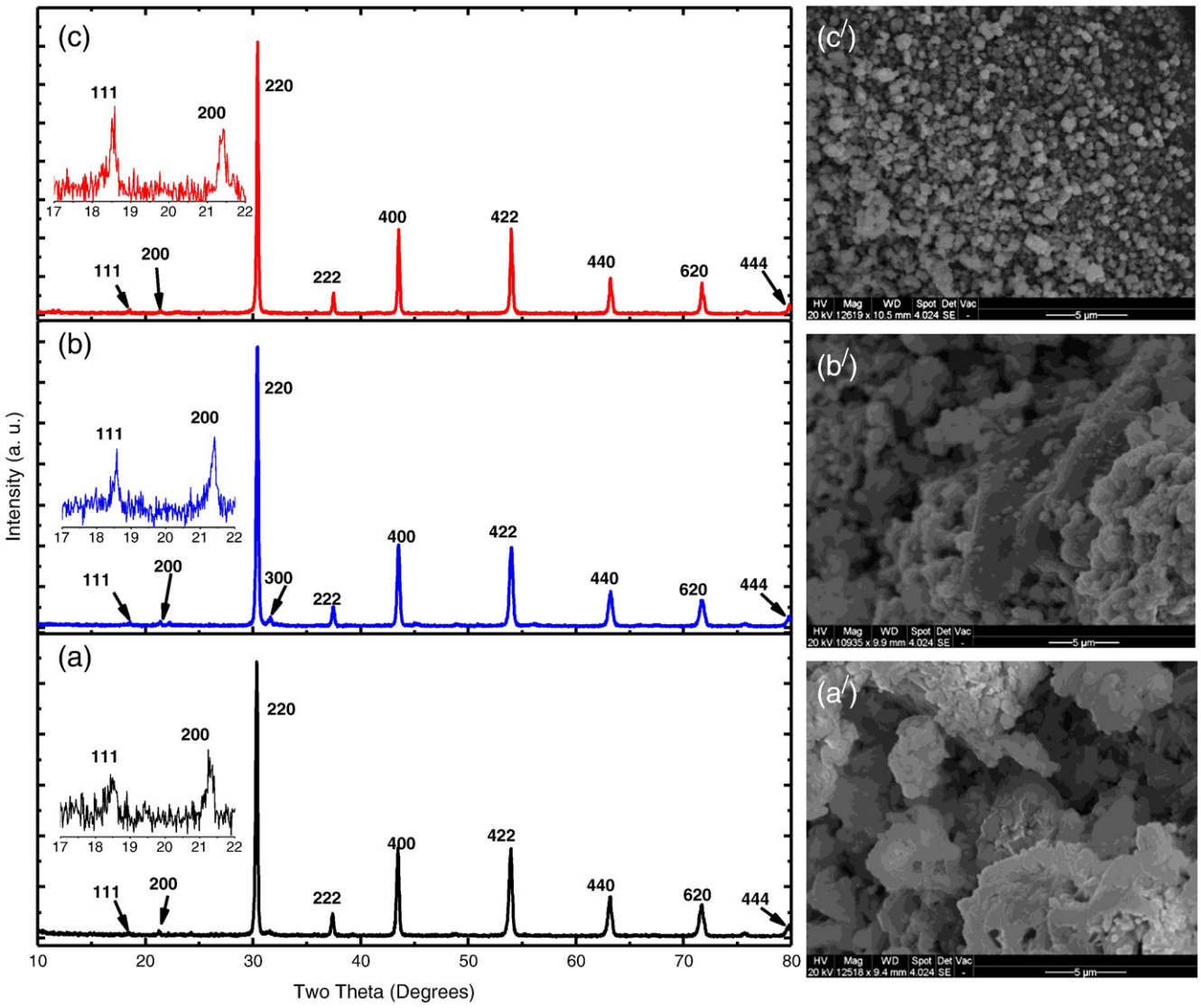

Fig. 1. Indexed powder X-ray diffraction (PXRD) patterns of $Ba_{1.75}K_{1.25}CaNb_2O_{9-\delta}$ (a) as-prepared, (b) sample 'a' heated at 700 °C for 5 days in CO_2, and (c) sample 'a' heated in boiling H_2O for 5 days. Insets show the selected area of PXRD. The SEM pictures of (a′) as-prepared, (b′) CO_2 treated and (c′) H_2O boiled $Ba_{1.75}K_{1.25}CaNb_2O_{9-\delta}$ are shown at the right-hand-side.

2. Experimental aspects

2.1. Synthesis of K-doped BCN

The double perovskite oxides with nominal chemical formula of $Ba_{2.5}K_{0.5}CaNb_2O_{9-\delta}$, $Ba_{2.25}K_{0.75}CaNb_2O_{9-\delta}$, $Ba_2KCaNb_2O_{9-\delta}$, and $Ba_{1.75}K_{1.25}CaNb_2O_{9-\delta}$ were prepared by employing solid-state (ceramic) reaction in air using appropriate amounts of high purity powder materials, such as $Ba(NO_3)_2$ (99+%, Alfa Aesar), $CaCO_3$ (99%, Fisher Scientific), Nb_2O_5 (99.5%, Alfa Aesar), and K_2CO_3 (99.85%, Alfa Aesar). The desired amount of 2-propanol was added to these starting powder materials in a zirconia bowl and ball milled (Pulverisette,

Table 1
Indexed powder XRD patterns of K-doped BCN sintered at 1100 °C.

h	*K*	*l*	$Ba_{2.5}K_{0.5}CaNb_2O_{9-\delta}$			$Ba_{2.25}K_{0.75}CaNb_2O_{9-\delta}$			$Ba_2KCaNb_2O_{9-\delta}$			$Ba_{1.75}K_{1.25}CaNb_2O_{9-\delta}$		
			$d_{(obs.)}$ (Å)	$d_{(calc.)}$ (Å)	$I_{(obs.)}$ (%)	$d_{(obs.)}$ (Å)	$d_{(calc.)}$ (Å)	$I_{(obs.)}$ (%)	$d_{(obs.)}$ (Å)	$d_{(calc.)}$ (Å)	$I_{(obs.)}$ (%)	$d_{(obs.)}$ (Å)	$d_{(calc.)}$ (Å)	$I_{(obs.)}$ (%)
1	1	1	4.822	4.823	2	4.818	4.811	2	4.808	4.803	2	4.792	4.793	3
2	0	0	4.176	4.177	4	4.168	4.167	3	4.180	4.159	3	4.157	4.151	4
2	2	0	2.953	2.954	100	2.946	2.946	100	2.941	2.941	100	2.936	2.935	100
2	2	2	2.411	2.412	10	2.406	2.406	9	2.403	2.401	8	2.398	2.397	7
4	0	0	2.088	2.089	31	2.083	2.083	30	2.081	2.080	33	2.076	2.076	30
4	2	2	1.705	1.705	32	1.701	1.701	31	1.698	1.698	32	1.694	1.695	27
4	4	0	1.477	1.477	13	1.473	1.473	13	1.470	1.471	15	1.467	1.468	12
6	2	0	1.321	1.321	11	1.318	1.318	11	1.315	1.315	12	1.312	1.313	10
4	4	4	1.206	1.206	3	1.202	1.209	4	1.201	1.208	4	1.199	1.198	3
			$a = 8.354(1)$ Å			$a = 8.333(1)$ Å			$a = 8.319(8)$ Å			$a = 8.302(1)$ Å		