Effect of Ba Nonstoichiometry in $Ba_x(Zr_{0.8}Y_{0.2})O_{3-\delta}$ on the Population of 5-Coordinated Y

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Introduction

In the proton conducting $Ba(Zr_{1-z}Y_z)O_{3-z/2}$ ceramics, a single oxygen vacancy in the perovskite materials can incorporate 2 protonic defects through a hydration process with a water molecule. Cation nonstoichiometry, which can be generated easily by the evaporation of BaO during sintering at high temperatures, is one of the major issues related to the proton transport properties of yttrium-doped barium zirconates. In this work, $Ba(Zr_{0.8}Y_{0.2})O_{3-\delta}$ samples with excess and deficient nominal Ba contents were investigated with X-ray diffraction (XRD) and ^{89}Y nuclear magnetic resonance (NMR) spectroscopy to observe the influence of Ba contents on the phase development, the locations of Y^{3+} in the lattice, and the oxygen vacancies next to Y^{3+} ions in the samples.[1]

Experimental

$Ba_x(Zr_{0.8}Y_{0.2})O_{3-\delta}$ pellets (10 mm in diameter) of x = 0.97, 1.0, 1.03 and 1.06 were synthesized by the solid state reaction route at 1600°C for 10 h in air. In order to minimize the evaporation of Ba, the pellets were covered with atmosphere powders that had the same compositions as the pellets. The Ba loss during the synthesis was analysed using an X-ray fluorescence spectrometer and the phase identification of the pellets was conducted using X-ray diffraction. For the ^{89}Y NMR analysis, 830 MHz NMR instrument at National High Magnetic Field Lab., FL, USA was used.

Results and Discussion

XRD patterns for $Ba_x(Zr_{0.8}Y_{0.2})O_{3-\delta}$ powder samples, from both pellets and atmosphere powders, showed that the signals are split into 2 peaks indicating the co-presence of two perovskite phases, which are the yttrium-substituted $BaZrO_3$ (BZY) and the $BaZrO_3$-like phase (BZ). As the starting Ba content was increased in the pellets and atmosphere powders, the amount of the BZY phase was enhanced and that of the BZ-like phase was depleted. The chemical composition of the samples analyzed by XRF showed that BaO vaporized continuously during the sintering.

The NMR analysis as shown in Fig. 1 indicated that the relative peak area of the 5-coordinated ^{89}Y was enhanced from 35 ± 7% to 49 ± 5% for the powder samples from the pellets as this Ba content increased. For the atmosphere powders with a lower starting Ba content, the relative peak area of the 5-coordinated ^{89}Y was reduced to 23 ± 8%. Stoichiometrically, reduced Ba contents (resulting from BaO evaporation) are supposed to generate more 5-coordinated Y^{3+} ions. In contrast, the ^{89}Y NMR data show that more 5-coordinated Y^{3+} ions are produced at higher Ba contents.

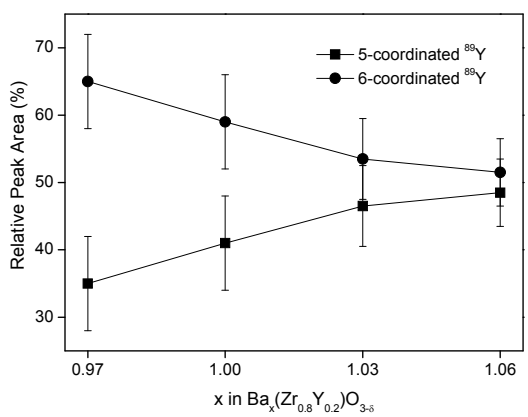

Fig.1 Relative NMR peak area of the 5-coordinated ^{89}Y for the powder samples from the $Ba_x(Zr_{0.8}Y_{0.2})O_{3-\delta}$ pellets with different Ba contents (x = 0.97, 1.00, 1.03, and 1.06 in the starting composition.

Conclusions

The population of the 5-coordinated Y^{3+} ions is related to the oxygen vacancy density. The depletion of the Ba contents by 9 at% in a starting composition reduced the 5-coordinated Y^{3+} ions from 49 ± 5 to 35 ± 7 %, suggesting the importance of maximizing the Ba contents in order to increase the oxygen vacancy population in BZY. The Y^{3+} ions were confirmed to replace Zr^{4+} ions as expected.

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References

[1] Lee, J.H., *et al.,* Journal of the American Ceramic Society, published online on 4 Aug 2014.