Influence of doping on the structural transformations of the proton conducting perovskite $BaCe_{1-x}Y_xO_{3-\delta}$

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Abstract.

From neutron diffraction it is known that the $BaCeO_3$ perovskite undergoes a sequence of phase transformations from high temperature cubic C to rhombohedral R, to orthorhombic O1 (*Imma*) and to orthorhombic O2 (*Pnma*). Doping Y^{3+} on the Ce^{4+} site introduces charge compensating O vacancies (V_O) that may be partially filled with OH complexes with exposition to H_2O, so making the material an ionic conductor.

Anelastic relaxation experiments have been carried out on samples doped with 2%Y and 10%Y; the real part $s'(T)$ of the complex elastic compliance presents softenings at the transitions, and the loss s''/s' curves allow the content of V_O and H to be monitored.

Doping has a strong effect on the temperature of the *Pnma/R* transition: with 10%Y in the fully hydrated state T_{O1-R} increases up to 750 K while after full outgassing falls to 500 K, meaning that the introduction of ~5% V_O shifts the transition of 250 K. While the effect of cation substitution on the transitions temperature is easily explained in terms of simple arguments usually valid for perovskites based on bond length considerations, the remarkable stabilization of the R phase by V_O requires to take into account the anomalous sequence of phase transitions of undoped $BaCeO_3$, where the R structure transforms into orthorhombic *Pnma* on cooling with the loss of an octahedral tilt system.

Introduction

Cerium-based perovskites oxides are a family of materials that, with appropriate doping, exhibit ionic conductivities of both O vacancies and protons and therefore are suitable for intermediate and high temperature applications such as fuel cells, gas sensors and other electrochemical devices. Yttrium-doped barium cerate, $BaCe_{1-x}Y_xO_{3-\delta}$ (BCY), with a fraction x of Ce^{4+} substituted with the

trivalent rare earth Y, contains a molar concentration $\delta = x/2$ of V_O for charge compensation, which may be filled with (OH)⁻ ions after reaction with a humid atmosphere at moderate temperatures. Therefore, BCY is an ionic conductor where the mobile species are both protons and V_O [1], and is also considered as a material in which the effect of V_O on the elastic properties can be conveniently studied [2, 3].

The temperature of the phase transformations of $BaCeO_3$ have been determined by neutron diffraction [4]: the perovskite lowers its symmetry from cubic (C) to rhombohedral (R) at $T_{R-C} = 1174$ K, to orthorhombic (O1, *Imma*) at $T_{O1-R} = 673$ K and to orthorhombic (O2, *Pnma*) at $T_{O2-O1} = 563$ K.

In this paper we present measurements of the complex elastic compliance $s(\omega,T) = s'+is''$ of BCY with $0 \leq x \leq 0.1$ at acoustic frequencies under various hydration levels and therefore different concentrations of V_O. The temperature range is between 300 and 1300 K and therefore includes the three structural transformations observed in undoped $BaCeO_3$.

Sample preparation and experimental details

The samples were prepared as described in Ref. 5, with starting powders prepared by auto-combustion synthesis and crystallization in air at 1000 °C for 5 h. The powders were isostatically pressed at 200 MPa into ingots, which were sintered at 1500 °C for 10 h, resulting in a final density of 5.54 g/cm³

The dynamic elastic compliance (susceptibility) $s(\omega,T) = s'+is''$, or its reciprocal the dynamic Young's modulus $E(\omega,T) = s^{-1}$, was measured by electrostatically exciting the flexural modes of the bars suspended in vacuum on thin thermocouple wires in correspondence with the nodal lines; the first and the third mode could be measured, whose frequencies are in the ratios 1:5.4, the fundamental frequencies being 1.5 kHz. The real part of the Young's modulus is related to the resonance angular frequency through $\omega_n = \alpha_n \sqrt{E'/\rho}$, where α_n is a geometrical factor of the nth vibration mode and ρ the mass density. The latter varies with temperature much less than E', so that $\omega^2(T)/\omega^2(T_0) \cong E(T)/E(T_0) = s(T_0)/s(T)$. The elastic energy loss coefficient, or the reciprocal of the mechanical quality factor [6], is $Q^{-1}(\omega,T) = s''/s' = E''/E'$; the Q^{-1} was measured from the decay of the free oscillations or from the width of the resonance peak.

Results and discussion

Figure 1 presents the anelastic spectrum of a sample of undoped $BaCeO_3$ measured on heating at ~1.5 kHz. The real part s' presents three main features at temperatures which are in good agreement with those determined by neutron diffraction [4] for the three phase transitions.
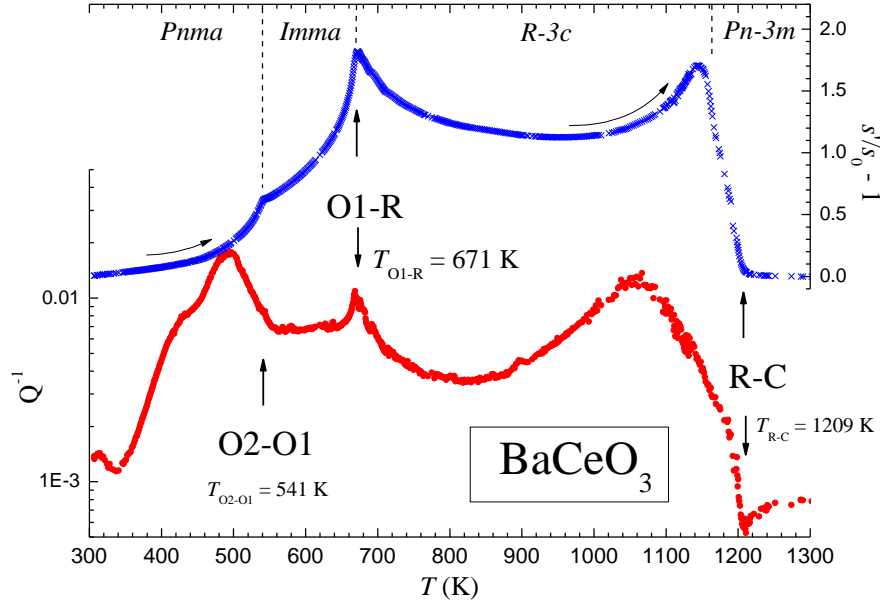
Fig. 1 Elastic compliance *s'* and energy loss coefficient Q^{-1} of undoped BaCeO₃.

The real part of the elastic compliance clearly shows a step at T_{R-C} suggesting that the order parameter is not the strain, since in this case one should observe a peak in the susceptibility [7]. Indeed, as we will discussed later, the order parameter should be the rotations of the O-octahedra.

By repeating the measurements on cooling it turns out that the transformations O1-R and O2-O1 present hysteresis (22 K and 4 K, respectively), indicating that they are first order; we can observe that O1-R must be first order since the lower temperature symmetry is not a subgroup of the rhombohedral one. The fact that the elastic compliance shows a peak at both T_{O1-R} and T_{O2-O1} can suggest the presence of dynamic fluctuations due to coupling between the soft mode responsible for the structural instability and the acoustic modes, which determine the elastic constants [8,9].

The anelastic spectra at different frequencies (not reported here) allow an easy identification of the thermally activated relaxations, and indicated that the two maxima in the elastic energy dissipation, Q^{-1}, at 495 K and 1055 K are probably due to the thermally activated motion of the domain walls associated with the product phases. In what follow we will concentrate on the anelastic effect connected with the phase transitions.

In order to study the effect of $Y^{3+} \rightarrow Ce^{4+}$ substitution on the structural stability of the perovskite, we measured samples with different amounts of doping, ranging from $x = 0$ to $x = 0.1$. Figure 2 shows the relative variations of the real part of the elastic compliance as a function of temperature at two different Y concentration. Although the anelastic spectra do not tell between which structures the transitions occur, they do not show any substantial change of the structural evolution on doping with Y; only the temperatures of the transitions are shifted.

The curves of Fig. 2 (upper part) refer to the samples in the fully hydrated state, when the V_O content should be very low. The highest temperatures reached during these measurements are below T_{R-C}, but the effect of doping on T_{O1-R} is quite clear: with 10%Y, T_{O1-R} shifts to higher temperature.
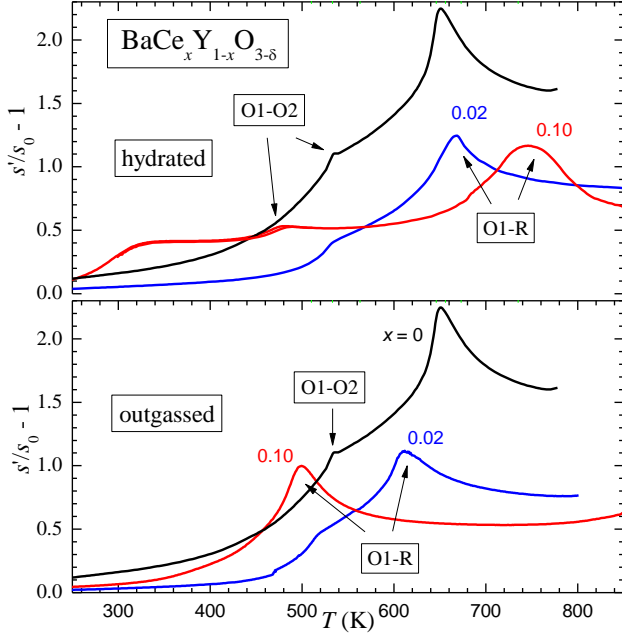
Fig. 2 Elastic compliance s' of BCY at various Y concentration, measured at ~1.5 kHz in the outgassed (upper panel) and hydrated (lower panel) state.
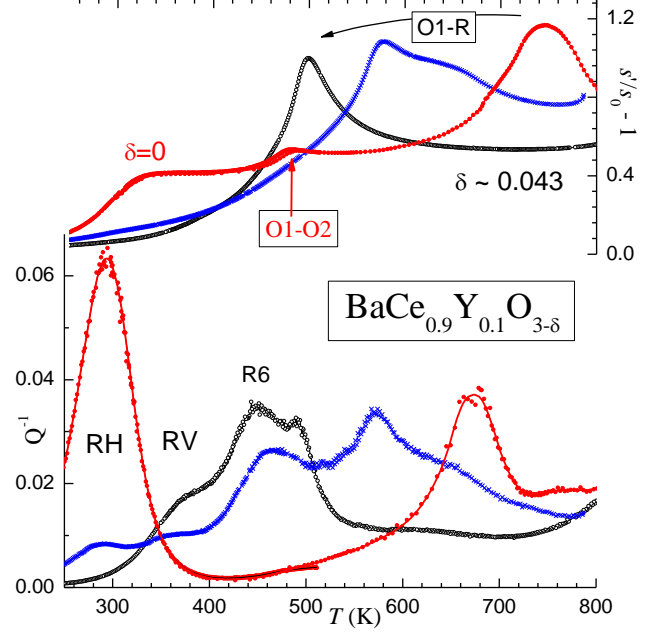
Fig. 3 Elastic compliance s' and energy loss Q^{-1} of 10%Y doped barium cerate at various O vacancies concentrations.

This result can be explained in terms of the O octahedral tilting which give rise to the decrease of symmetry at the phase transitions. In particular, the undistorted octahedra should tilt around all the three axes at T_{R-C} ($a^0a^0a^0 \rightarrow a^-a^-a^-$ in Glazer's notation [10]), the tilt pattern changes loosing a rotation at T_{O1-R} ($a^-a^-a^- \rightarrow a^0b^-b^-$) and a rotation around the a axis reappears at T_{O1-R} ($a^0b^-b^- \rightarrow a^+b^-b^-$). The tilts are due to the mismatch introduced from the Y^{3+} ions which are larger than the Ce^{4+} ones and the measure of the mismatch can be given through the Goldschmidt tolerance factor, t, which is a geometrical factor composed of the radii of the three atoms in the structure; $t = (R_A - R_O)/\sqrt{2}(R_B - R_O)$, where R_A, R_B, and R_O are the ionic radii of the A site and B site cations and the O ion respectively ($t = 1$ in the cubic undistorted ABO_3 perovskite structure). By doping with Y, t decreases and the enhanced driving force for tilting is expected to increase the transition temperatures.

The lower part of Fig. 2 shows that the O vacancies produce a much stronger effect on the transition temperature T_{O1-R}. In fact, when hydrating, each molecule of water fills one V_O and provides two H^+ atoms that may diffuse among the O^{2-} ions, to which are bound as $(OH)^-$. As a consequence, by outgassing the hydrated samples, the protons concentration decreases and concomitantly the V_O content increases. Such concentrations can be monitored via the anelastic spectra thanks to the presence of two thermally activated relaxations, labelled as RH and RV in Fig. 3, which are connected with H and V_O jumps and whose intensities are therefore proportional to the respective concentrations [5]. We will not analyse here these relaxations, but the maximum concentration of V_O was estimated for the 10%Y sample as $\delta_{max} = 0.043$ from the weight change of the sample between fully outgassed (up to 730 °C in vacuum $< 10^{-5}$ mbar) and fully hydrated (1-2 h at 520 °C in 50 - 100 mbar H_2O followed by slow cooling). The temperatures for both the O1-R and the O2-O1 transitions deduced from figure 2 are reported in Table 1.

Table 1. Temperatures of the O1-R and O1-O2 phase transformations.

	T_{O1-R}	T_{O2-O1}

	(K)	(K)
$x = 0$ - hydrated	671	541
$x = 0.02$ - hydrated	667	534
$x = 0.10$ - hydrated	746	480
$x = 0.02$ - outgassed	611	517
$x = 0.10$ - outgassed	498	?

At the highest Y concentration, in the outgassed sample the O1-R is shifted at a temperature lower of about 250 K with respect to T_{O1-R} in the hydrated state. Figure 3 shows the anelastic spectra also at an intermediate step of outgassing, giving confidence that indeed O1-R has shifted to around 500 K, which is close to T_{O2-O1} in the hydrated state. At higher Y doping the R phase is expected to extend to still lower temperature, in agreement with the observation that the room temperature structure changes from orthorhombic to rhombohedral in dehydrated samples with $x > 0.15$ [11].

The effect of outgassing on O2-O1 is more difficult to assess, since for the sample with 10% Y such a transition is no more recognizable due to the overlapping with the O1-R and with an intense thermally activated peak (R6 in Fig. 3).

The influence of the V_O on the structure of BCY is not easily interpreted only on the basis of the tolerance factor. In fact, filling the vacancy is expected to increase the lattice parameter [12] and if this causes an increase of t too, then T_{O1-R} should decrease, but the opposite is true.

Finally, the ordering of V_O into different sublattices may play a role [13], but V_O ordering cannot be the direct cause of stabilization of the O1 phase, since O1-R occurs also when most V_O are filled and since T_{O1-R} is depressed by V_O.

Conclusions

The effect of $Y^{3+} \rightarrow Ce^{4+}$ substitution on the structural stability of the ionic conducting perovskite $BaCe_{1-x}Y_xO_{3-\delta}$ have been studied by measuring the anelastic spectra of samples with different amount of doping, ranging from $x = 0$ to $x = 0.1$. In addition, the content of both H atoms and O vacancies have been varied by hydrating at different levels the samples. It turns out that the larger ionic radius of Y with respect to Ce can explain the increase of the temperature of the orthorhombic to rhombohedral phase transition observed when the samples are fully hydrated. On the other hand such a transitions is strongly shifted to lower temperature by increasing the content of O vacancies and this fact is not easily explained in terms of simple arguments usually valid for perovskites.

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