

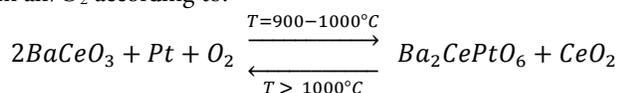
Oxidative Platinum Uptake for BaCeO₃ at High Temperatures

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The proton conductor BaCeO₃^{1,2} can be doped with a wide variety of B³⁺ cations belonging to the lanthanides and scandium, indium and yttrium. The reported experiment focussed on the oxidative platinum uptake in BaCeO₃ and its doped analogues at approximately 900 °C in the presence of O₂. The original discovery of the formation of a transient Ba₂CePtO₆ B-cation ordered double perovskite by Ouchette³ proposed an oxidative uptake of platinum by BaCeO₃. We originally observed in our in-situ powder X-ray diffraction experiments the occurrence of transient diffraction peaks between 900 °C and 1000 °C. Those peaks could be explained by either decomposition of BaCeO₃ or the uptake of platinum (BaCeO₃ or BaCe_{0.8}In_{0.2}O_{3-δ} was mounted directly on a Pt heater during the in-situ X-ray diffraction experiments) with the formation of a double perovskite. Our diffraction experiments showed that the transient diffraction peaks are observed in the presence of oxygen. In contrast no transient peaks were observed when reacting BaCeO₃ and platinum in the absence of oxygen (dynamic vacuum). Therefore a redox process was considered the likely origin of those additional peaks.

Our experiments showed that BaCeO₃ and the indium doped analogue (Ba₂Ce_{0.8}In_{0.2}O_{3-δ}) is capable of oxidative uptake of metallic platinum at temperatures as low as 900 °C in air/O₂ according to:



Furthermore the Pt is reductively released at temperatures above 1000 °C.

For the powder neutron diffraction experiment BaCe_{0.8}In_{0.2}O_{3-δ} was placed together with platinum foil in a quartz tube and backfilled with oxygen before sealing. The second sample was prepared similarly but without any platinum. The samples were heated from room temperature to 1050 °C on neutron powder diffractometer C2. The variable temperature data are shown in figure 2 and clearly illustrate significant platinum uptake as indicated by the (200) reflection for the platinum containing sample. This clearly illustrated that platinum was oxidatively added to the BaCe_{0.8}In_{0.2}O_{3-δ} phase and resulted in the B-cation ordered double perovskite Ba₂Ce_{0.8}In_{0.2}PtO_{6-δ}.⁴

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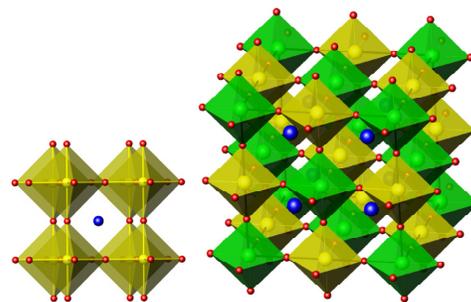


Figure 1: Left structure: Simple cubic perovskite (space group: *Pm-3m* at high temperatures) BaCe_{0.8}In_{0.2}O_{3-δ}. Right structure: Cubic double perovskite (space group: *Fm-3m*) BaCe_{0.8}In_{0.2}PtO₆ as formed between 900 °C and 1000 °C in the presence of O₂. Blue = Ba²⁺, yellow = Ce⁴⁺/In³⁺, green = Pt⁴⁺, red = O²⁻.

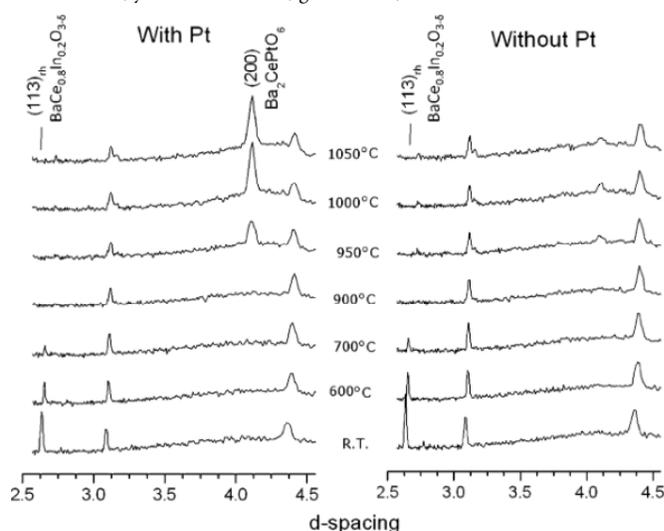


Figure 2: Variable powder neutron diffractograms collected on C2 at CNBC for the formation of BaCe_{0.8}In_{0.2}PtO_{6-δ}. Left panel: Growth of BaCe_{0.8}In_{0.2}PtO_{6-δ} phase above 900 °C from BaCeO₃ and platinum metal in an oxygen containing atmosphere as indicated by the appearance of the (200) peak for the face centered double perovskite. Right panel: No evidence of double perovskite formation above 900 °C.