Dual functional self-regenerative Cr-substituted $Ba_2In_2O_5$

M. Widenmeyer[1], S. Yoon[2], G. Chen[1], A. Weidenkaff[1,2]
[1] Technische Universität Darmstadt, Materials and Resources, 64287 Darmstadt, Germany
[2] Fraunhofer IWKS, 63457 Hanau, Germany

$Ba_2In_2O_5$ is a high-temperature oxide and proton conductor with mixed ionic-electronic conductivity[1]. In such materials ceramic membranes for oxygen gas separation is one of the interesting research areas[2]. The yellow colored powders suggest that it is potentially applicable as a photocatalyst for the activation of small molecules such as H_2O and CO_2[3,4]. The partial substitution of In^{3+} by Cr^{3+} altered the crystal structure and changed the optical bandgap. The crystal structure changes are important for membrane applications, while the resulting bandgap variations are relevant for photocatalyst applications.

Addition of Cr^{3+} induced a crystal structure change from *Ibm*2 to *I*4*cm* due to an enhanced disorder of oxygen vacancies. This increased disorder resulted in a reduced activation energy for oxygen transport *via* oxygen vacancies. However, more than 10 % Cr substitution for In caused a shrinkage of the unit cell resulting in a reduced self-diffusion coefficient of the oxide ions. Consequently, $Ba_2In_{1.8}Cr_{0.2}O_5$ exhibited the highest oxygen permeability with $P(O_2)$ = 1.4 mL·cm^{-1}·min^{-1}·mm at T = 1223 K (Fig. 1). Thermochemical studies showed an easy membrane material reformation using the end-of-lifetime phases also suggesting a potential self-regeneration behavior using a regular oxygen treatment[5].

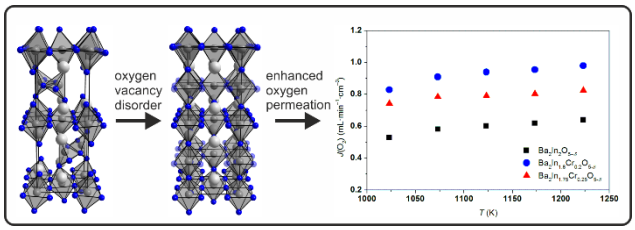

Figure 1: Crystal structure change / oxygen vacancy disorder (left) and oxygen permeability (right) [2].

Furthermore, increasing Cr^{3+} substitution reduced the bandgap and improved the photocatalytic conversion of CO_2 in presence of H_2. $Ba_2In_{1.4}Cr_{0.6}O_5$ exhibited a compatible photoactivity with that of reference P-25 (TiO_2) (Fig. 2), even though having a 250-times smaller BET surface area[4].

Even though Cr-substituted $Ba_2In_2O_5$ involves the usage of the critical element indium, it can be interesting to be used, since it allows high oxygen permeation at ca. 200 K lower T than classical membrane materials [2]. Additionally, the indium can be easily recovered in the material cycle, e.g. the recyclate of used membranes can be again applied as photocatalyst.

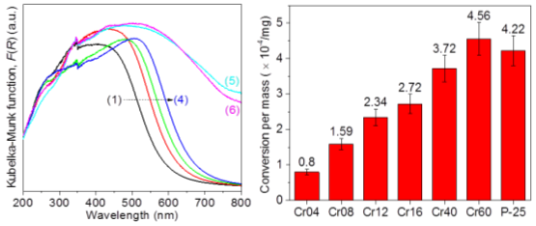

Figure 2: Optical bandgaps of $Ba_2In_{2-x}Cr_xO_5$ (left; x = 0.04 (1), 0.08 (2), 0.12 (3), 0.16 (4), 0.4 (5), 0.6 (6)) and photocatalytic CO_2 conversion compared with P-25 as reference material (right) [4].

[1] J. Goodenough et al., *Solid State Ionics* **52** (1992), 105.
[2] M. Widenmeyer et al., *J. Mem. Sci.* **595** (2020), 117558.
[3] S. Yoon et al., *Solid State Sci.* **73** (2017), 1.
[4] S. Yoon et al., *Solid State Sci*. **78** (2018), 22.
[5] M. Widenmeyer et al., *Thermochim. Acta* (2019) submitted.

Corresponding author: marc.widenmeyer@mr.tu-darmstadt.de