Dual Functional Self-Regenerative Cr-substituted $Ba_2In_2O_5$

Marc Widenmeyer[1]*, Songhak Yoon[2], Guoxing Chen[1], Anke Weidenkaff[1,2]*

[1] Technische Universität Darmstadt, Materials and Resources, Alarich-Weiss-Str. 2, 64287 Darmstadt, Germany

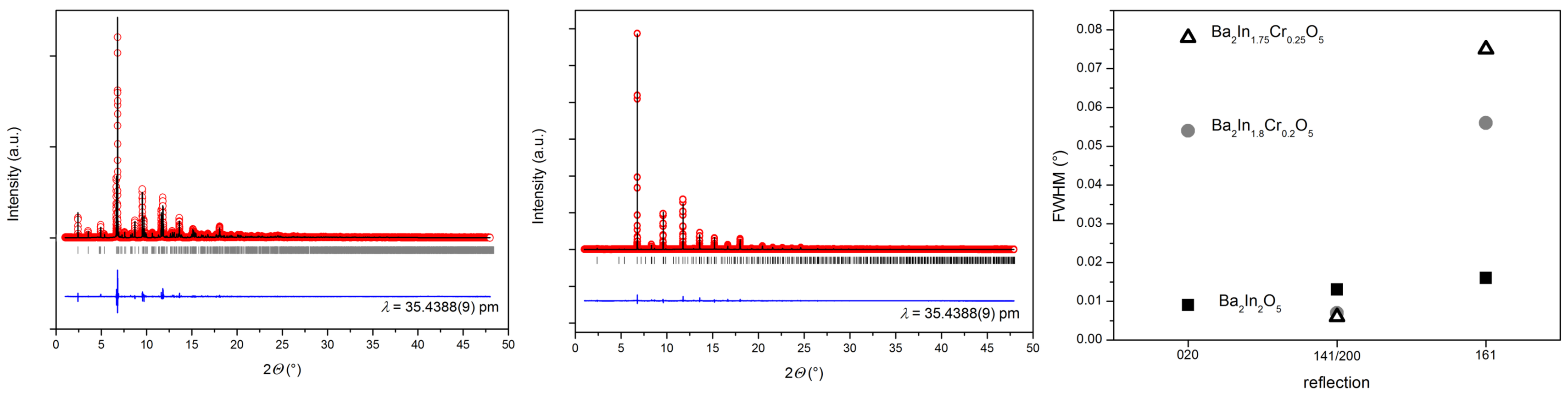
[2] Fraunhofer Institute IWKS, Rodenbacher Chaussee 4, 63457 Hanau, Germany

* marc.widenmeyer@mr.tu-darmstadt.de; anke.weidenkaff@mr.tu-darmstadt.de

Brownmillerite-type $Ba_2In_2O_5$ is a high-temperature proton conductor with mixed ionic-electronic conductivity. It shows a yellow color[1] and band gap of $E_G \approx 2.9$ eV[2]. These electronic and optical properties imply an application as oxygen transport membrane and photocatalyst for CO_2 reduction. Partial substitution of Cr^{3+} for In^{3+} allows a band gap reduction together with crystal structure changes crucial for the efficiency of the photocatalytic reaction[3] and the oxygen permeation performance of the ceramic membrane[4].

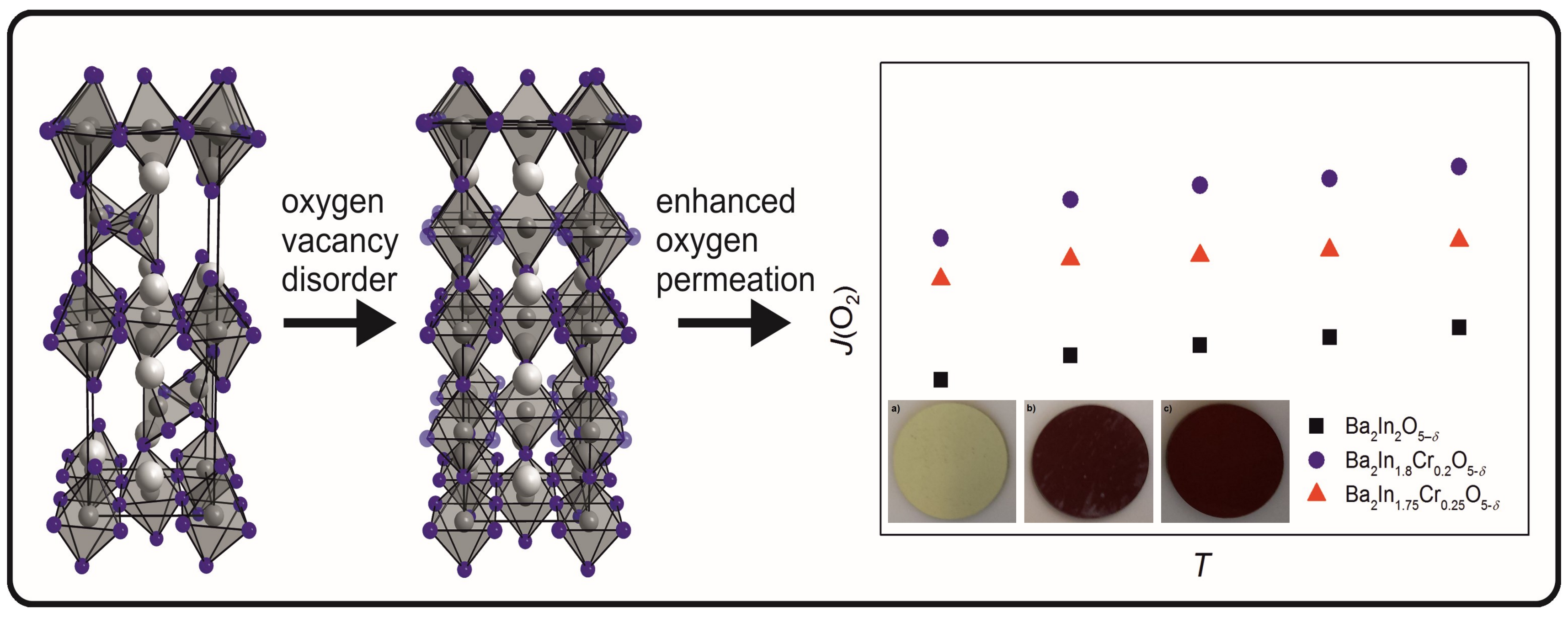
Oxygen Transport Membranes

The partial substitution of Cr^{3+} for In^{3+} causes O vacancy disorder[3,4]



Rietveld refinements of synchrotron diffraction data of $Ba_2In_{2-x}Cr_xO_5$: orthorhombic (*Ibm*2) $Ba_2In_2O_5$ (left), tetragonal (*I4cm*) $Ba_2In_{1.75}Cr_{0.25}O_5$ (middle), and changing of full width at half maximum (FWHM) for 3 representative reflections (right) [4].

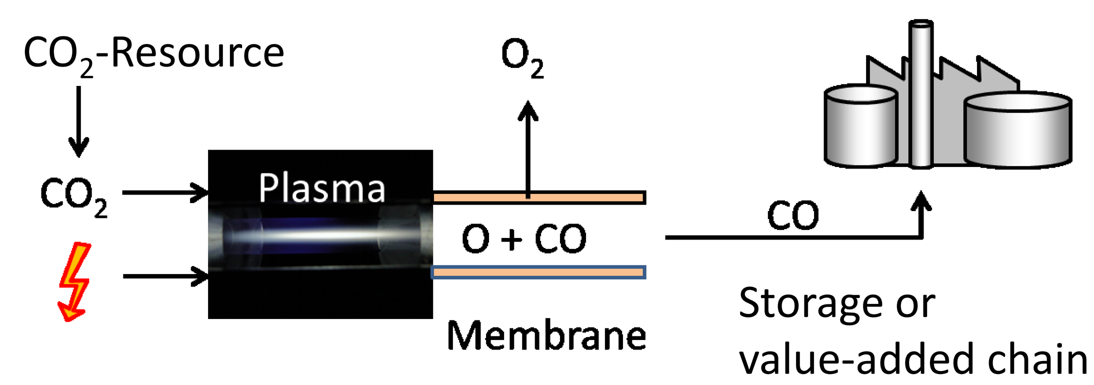
➔ FWHM of reflections along the ***c***-axis are a direct measure of O vacancy disorder.



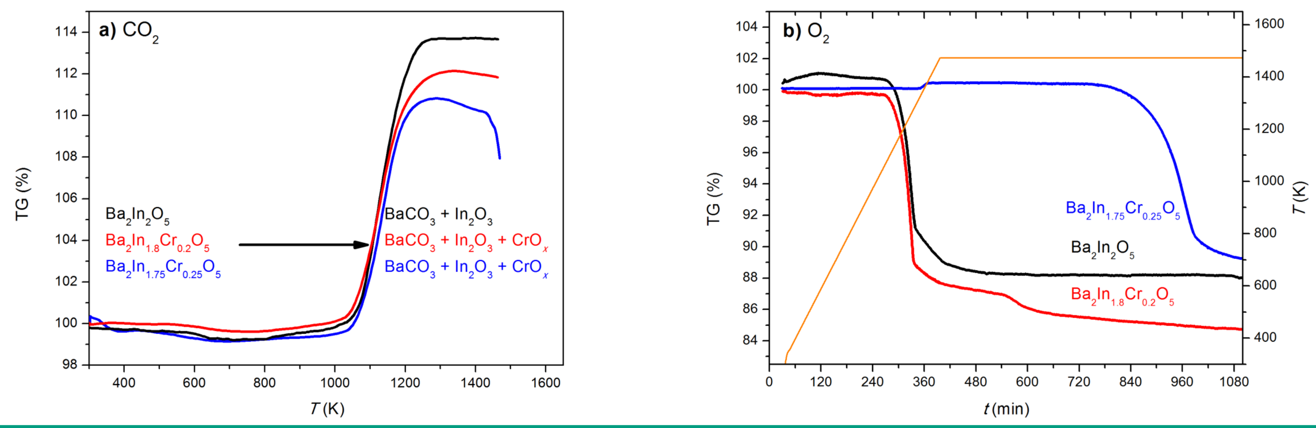
Structural changes of $Ba_2In_{2-x}Cr_xO_5$ and their effect on oxygen permeation flux $J(O_2)$: orthorhombic (*Ibm*2) $Ba_2In_2O_5$ (left), tetragonal (*I4cm*) $Ba_2In_{1.75}Cr_{0.25}O_5$ (middle), and temperature and composition dependent oxygen permeation flux $J(O_2)$ together with photos of sintered membranes of $Ba_2In_2O_5$ (a), $Ba_2In_{1.8}Cr_{0.2}O_5$ (b), and $Ba_2In_{1.75}Cr_{0.25}O_5$ (c) (right) [4].

x	$P(O_2$,1223 K) mL·min^{-1}·cm^{-2}·mm	E_A kJ·mol^{-1}	D_0 cm^2·s^{-1}
0.00	0.89	9.4	1.6
0.10	**1.40**	8.1	**2.2**
0.25	1.10	**4.9**	1.3

➔ O vacancy disorder reduces E_A
➔ Unit cell volume controls D_0
➔ x = 0.1 best compromise

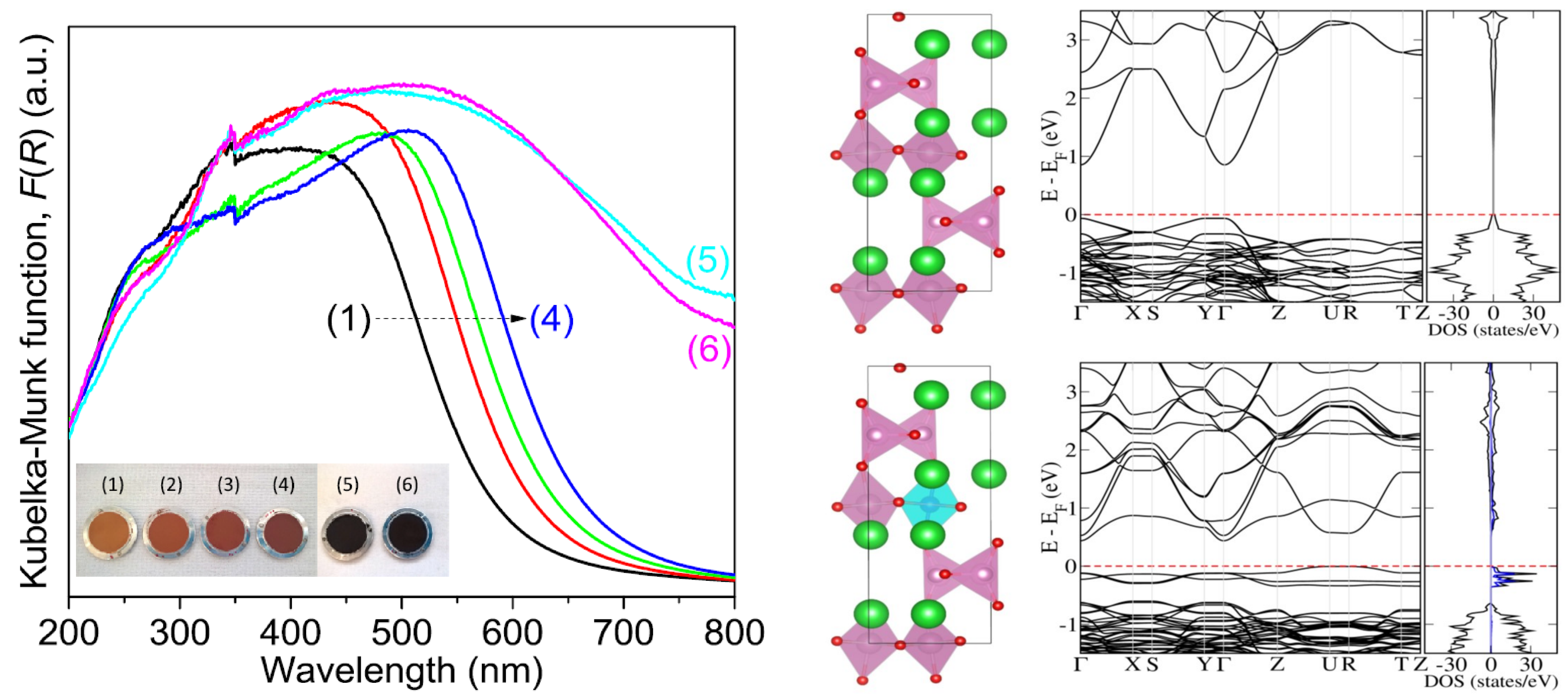


Concept of plasma-induced CO_2 conversion (top) and photo of an air plasma (bottom). Thermogravimetic (TGA) analysis of $Ba_2In_{2-x}Cr_xO_5$ in flowing CO_2 leading above $T \approx 1050$ K to a decomposition to the starting materials In_2O_3, $BaCO_3$, and chromium oxide **(a)**. This allows for a material reformation upon oxygen treatment (TGA) **(b)** [5].

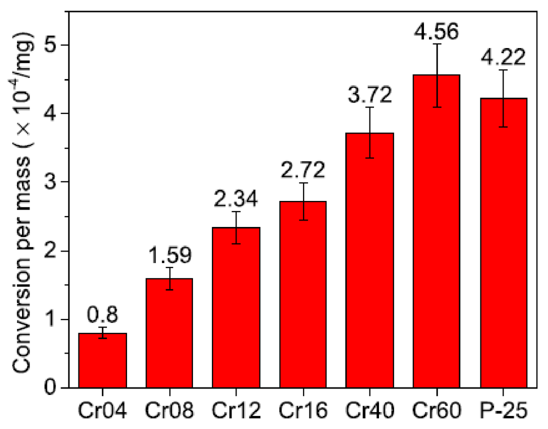


Photocatalytic CO_2 Reduction

$Ba_2In_{2-x}Cr_xO_5$ is able to convert CO_2 in presence of H_2 and UV/Vis.



Band gap of $Ba_2In_{2-x}Cr_xO_5$: Optical absorbtion spectra of (1) $Ba_2In_{1.96}Cr_{0.04}O_5$, (2) $Ba_2In_{1.92}Cr_{0.08}O_5$, (3) $Ba_2In_{1.88}Cr_{0.12}O_5$, (4) $Ba_2In_{1.84}Cr_{0.16}O_5$, (5) $Ba_2In_{1.60}Cr_{0.40}O_5$, (6) $Ba_2In_{1.40}Cr_{0.60}O_5$ (left), and calculated electronic band structure of $Ba_2In_2O_5$ and $Ba_2Cr_{1.75}Cr_{0.25}O_5$; green = Ba, pink = In, blue = Cr, red = O (right) [5]. XRD data of $Ba_2In_{1.40}Cr_{0.60}O_5$ showed the presence of small quantities of $BaCrO_4$.

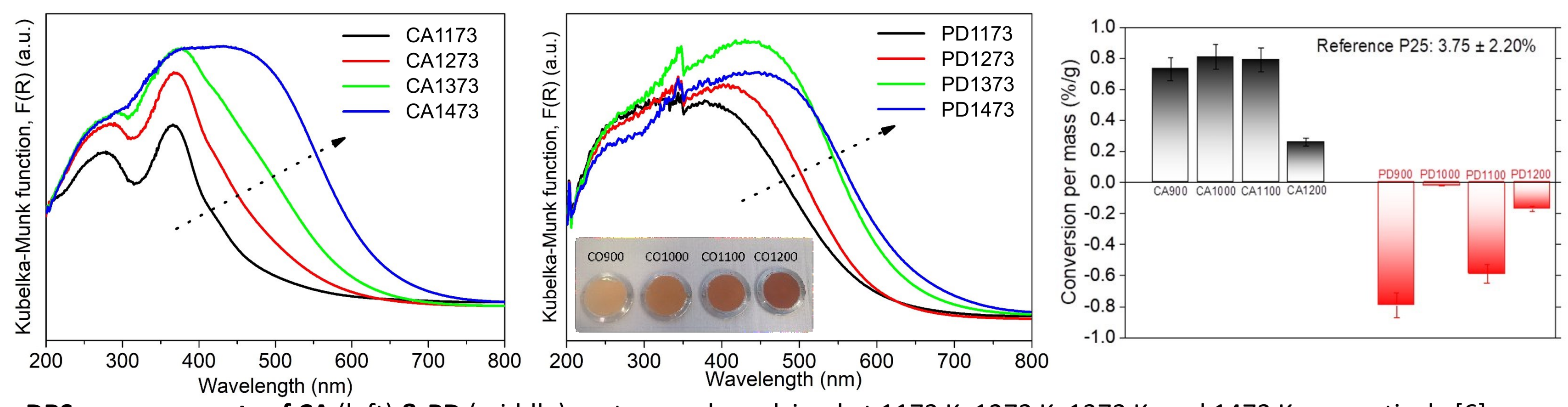


Photocatalytic conversion of CO_2 in presence of H_2: Conversion upon Hg lamp irradiation ($\lambda \leq 578$ nm) increases due to an narrowing of the band gap by Cr substitution. BET active surface area of $Ba_2In_{2-x}Cr_xO_5$ is by a factor of about 250 smaller than for P-25 [5].

➔ Using adjusted soft chemistry synthesis to enhance active surface area.

Soft Chemistry Synthesis Reaction Protocol

Precursors for Soft Chemistry: $Ba(NO_3)_2$, $In(NO_3)_3 \cdot y\,H_2O$, $Cr(NO_3)_2 \cdot 9\,H_2O$
→ **CA route:** Only citric acid (CA) as chelating agent or **PD route:** Additionally, 2,6-Pyridinedicarboxylic acid (2,6-pydc), 2,6-diaminopyridine (2,6-pyda) and polyethylene glycol (PEG) for complexation process
→ **Wet chemistry:** (i) Mixing, (ii) polyesterification, (iii) subsequent calcination at different temperatures



DRS measurements of CA (left) **& PD** (middle) route samples calcined at 1173 K, 1273 K, 1373 K, and 1473 K, respectively [6].
Photocatalytic CO_2 conversion (right): CA shows higher activity then solid state samples (for short time); PD shows no activity [6].

➔ Surface composition & structure is crucial for photocatalysis
➔ Surface reconstruction
➔ Reaction & deactivation mechanisms unknown

➔ Combined ***in operando*** **XANES/DRIFTS/MS studies** after EBS upgrade are required for an enhanced understanding of the fundamental reaction steps

References & Acknowledgements

[1] J. Goodenough *et al.*, *Solid State Ionics* **1992**, 52, 105–109.
[2] S. Yoon *et al.*, *Solid State Sci.* **2017**, *73*, 1–6.
[3] S. Yoon *et al.*, *Solid State Sci.* **2018**, *78*, 22–29.
[4] M. Widenmeyer *et al.*, **2019**, submitted.
[5] M. Widenmeyer *et al.*, **2019**, submitted.
[6] S. Yoon *et al.*, in preparation.

SPONSORED BY THE Federal Ministry of Education and Research

KOPERNIKUS PROJEKTE Die Zukunft unserer Energie

The funding of the *Federal Ministry of Education and Research of Germany* in the framework of the *Kopernikus Projects for the Energiewende* within the project *Plasma-induced CO_2-conversion* (project number: 03SFK2S3B), the *Vector Stiftung* (2015-044), and *ESRF*, Grenoble, France within experiment CH-5342 is highly acknowledged. We are thankful to *M.Sc. Katharina-Sophia Wiegers*, *Dr. Stefano Checchia*, *Dr. Mauro Coduri*, and *Prof. Dr. Marco Scavini* for sample preparation and data collection.