Experimental report

30/05/2021

Proposal:	**5-24-640**	**Council:**	10/2019

Title: Crystal Structure Determination ofBrownmillerite-type BaIn2-xCrxO5.(H2O)y Oxygen Transport Membranes and Photocatalysts

Research area: Materials

This proposal is a new proposal

Main proposer: **Marc WIDENMEYER**

Experimental team:
Stanislav SAVVIN
Simon KEILHOLZ
André GOETZE
Marc WIDENMEYER
Raphael FINGER

Local contacts:
Stanislav SAVVIN
Thomas HANSEN

Samples:
Ba2In2O5
Ba2In1.75Cr0.25O5

Instrument	Requested days	Allocated days	From	To
D2B	3	2	09/09/2020	11/09/2020
D20	0	1	16/02/2021	17/02/2021

Abstract:

Brownmillerite-type Ba2In2O5 is a well-known mixed ionic electronic conductor material with yellow color (EG ~2.9 eV). Due to the high affinity to water incorporation fast proton conduction is observed below ~600 K. Considering the Brownmillerite structure as defect-perovskite structure with an intrinsically large number of oxygen vacancies a promising oxide ion transport ability of the material is implied. Additionally, the material is found to be suitable for photocatalytic CO2 splitting due to proper active sites (which are currently not clearly identified) and band positions. The conversion efficiency is still low mainly due to the rather large band gap. The band gap can be reduced by partial substitution of In by Cr, hence boosting the CO2 conversion. This substitution causes additional structural changes leading to a high degree of disorder of the oxygen vacancies increasing the oxygen permeation by nearly 40 % compared to pristine Ba2In2O5. Open questions remain regarding the correct assignment of space groups and the nature of the anionic sublattice.

Crystal Structure Determination of Brownmillerite-type $BaIn_{2-x}Cr_xO_5\cdot(H_2O)_y$ Oxygen Transport Membranes and Photocatalysts (5-24-640)

Marc Widenmeyer, Anke Weidenkaff, Technical University of Darmstadt, Darmstadt, Germany
Songhak Yoon, Fraunhofer Research Institution IWKS, Hanau, Germany
Raphael Finger, Holger Kohlmann, Leipzig University, Leipzig, Germany

Two brownmillerite-type samples, namely $Ba_2In_2O_5\cdot 0.16H_2O$ and $Ba_2In_{1.8}Cr_{0.2}O_5\cdot 0.74H_2O$, have been measured at 10 K and 300 K on D2B with an incident wavelength of 1.594 Å for a determination of oxygen content and H positions. The low temperature is used to reduce the thermal motion of the H_2O molecules. The sample $Ba_2In_{1.8}Cr_{0.2}O_5\cdot 0.74H_2O$ was transferred to D20 (wavelength: 1.86500(3) Å) and was placed in a leuco-sapphire crucible to separate the powder from the Nb wall of the can. Then it is heated from RT to 1573 K using a high temperature furnace with Nb heaters to investigate the dehydration behavior and a potential phase transition from tetragonal to cubic structure.

Comparing the neutron diffraction data of $Ba_2In_2O_5\cdot 0.16H_2O$ and $Ba_2In_{1.8}Cr_{0.2}O_5\cdot 0.74H_2O$ at RT, the later showed a higher background in good accordance with expectations based on the higher water content (incoherent scattering of ^1H). In agreement with synchrotron data[1],[2] Rietveld refinements in *Icmm* and *I4cm*, respectively, successfully reproduced the collected diffraction data. However, additional small reflections from secondary phase(s) have been observed in both cases. For $Ba_2In_{1.8}Cr_{0.2}O_5\cdot 0.74H_2O$ one secondary phase was identified as $BaIn_2O_4$. During cooling to 10 K no structural changes have been observed with exception of thermal expansion and oxygen content. The effect of a differing oxygen content might be resulted from a consequence of at least one unknown phase and/or other contributions from the sample environment. These structure models have been setup without considering the H atoms. At 10 K data points at around $2\Theta = 48°$ and above 150° had to be cut out due to a contribution of the cryofurnace. Even at 10 K diffraction patterns did not show any signs of a localization of H atoms. Difference Fourier maps have been tested to locate the ^1H atoms, typically rather straight-forward due to the negative coherent scattering power of ^1H. However, the signal-to-noise ratio seems to be insufficient to provide a clear picture. In addition, still, several reflections, occurring in both measurements at the same position with no temperature dependent shift are observed.

During the high temperature experiment on $Ba_2In_{1.8}Cr_{0.2}O_5\cdot 0.74H_2O$ several regions had to be cut out since they contain reflections of the highly textured Nb foil and can, respectively, hamper an evaluation of the diffraction data in these angular ranges. Besides, several regions needed to be excluded due to a contribution of the used sapphire crucible at elevated temperatures. Further, two reflections at about $2\Theta = 135°$ were not evaluated as they do not shift in temperature and no sample reflection is expected in this area. In contrast to the reports on $Ba_2In_2O_5$ (T_c = 1313 K)[3] for $Ba_2In_{1.8}Cr_{0.2}O_5\cdot 0.74H_2O$ a phase transition to the cubic defect perovskite-type was not observed up to 1573 K, which is interesting since the partial substitution of In for Cr results in an enhanced disordering of the brownmillerite-type structure, so one might at a first glance expect an easier transition to a fully oxygen vacancy disordered perovskite-type structure. However, it has to be kept in mind that such a phase transition might be also hampered by the presence of Cr^{6+} next to In^{3+}, since Cr^{6+} is not in favor of a (pseudo-)octahedral coordination environment as provided by a perovskite-type structure. In addition, massive octahedral distortion would be needed to host the large size mismatch between Cr^{6+} and In^{3+}. During heating in accordance with TGA data[4] first a release of the contained H_2O was observed. This can be seen by a lowering of the background (due to a reduction of incoherent scattering of ^1H) and additionally by expansion and contraction of the unit cell below 600 K as earlier observed by synchrotron diffraction[2]. Overall, a detailed evaluation of the *in situ* diffraction data is rather challenging with respect to the limited scattering lengths of In (b_c = 4.065 fm) and Cr (b_c = 3.635 fm), respectively, and the significant absorption capability (σ_a = 194 barns) of In for thermal neutrons. In combination with other X-ray and neutron studies not published yet, the oxygen content seems higher than 5, which is unexpected for brownmillerite-type phases. However, for the chromium-substituted sample assuming an oxidation state +6 for Cr as obtained by XPS in $Ba_2In_{2-x}Cr_xO_{5+y}$[5], instead of In^{3+}, an oxygen content of 5.3 is expected. At 1573 K, the oxygen content could be refined to 5.19(4). Near room temperature, the expected oxygen content is around 5.3 within standard deviations. Overall, due to the above issues, the question of a potential phase transition to cubic could not been answered.

In summary, the thermal behavior of $Ba_2In_2O_5{\cdot}0.16H_2O$ between 10 K and 293 K has been studied and no H atoms could be localized using Fourier Maps. The same is true for $Ba_2In_{1.8}Cr_{0.2}O_5{\cdot}0.74H_2O$. Still, several areas with negative scattering contribution around the oxygen could be identified, despite the collected diffraction data showed no localization of these atoms. Further, no structural change affecting the symmetry of the crystal structure between 10 K and 1573 K could be observed.

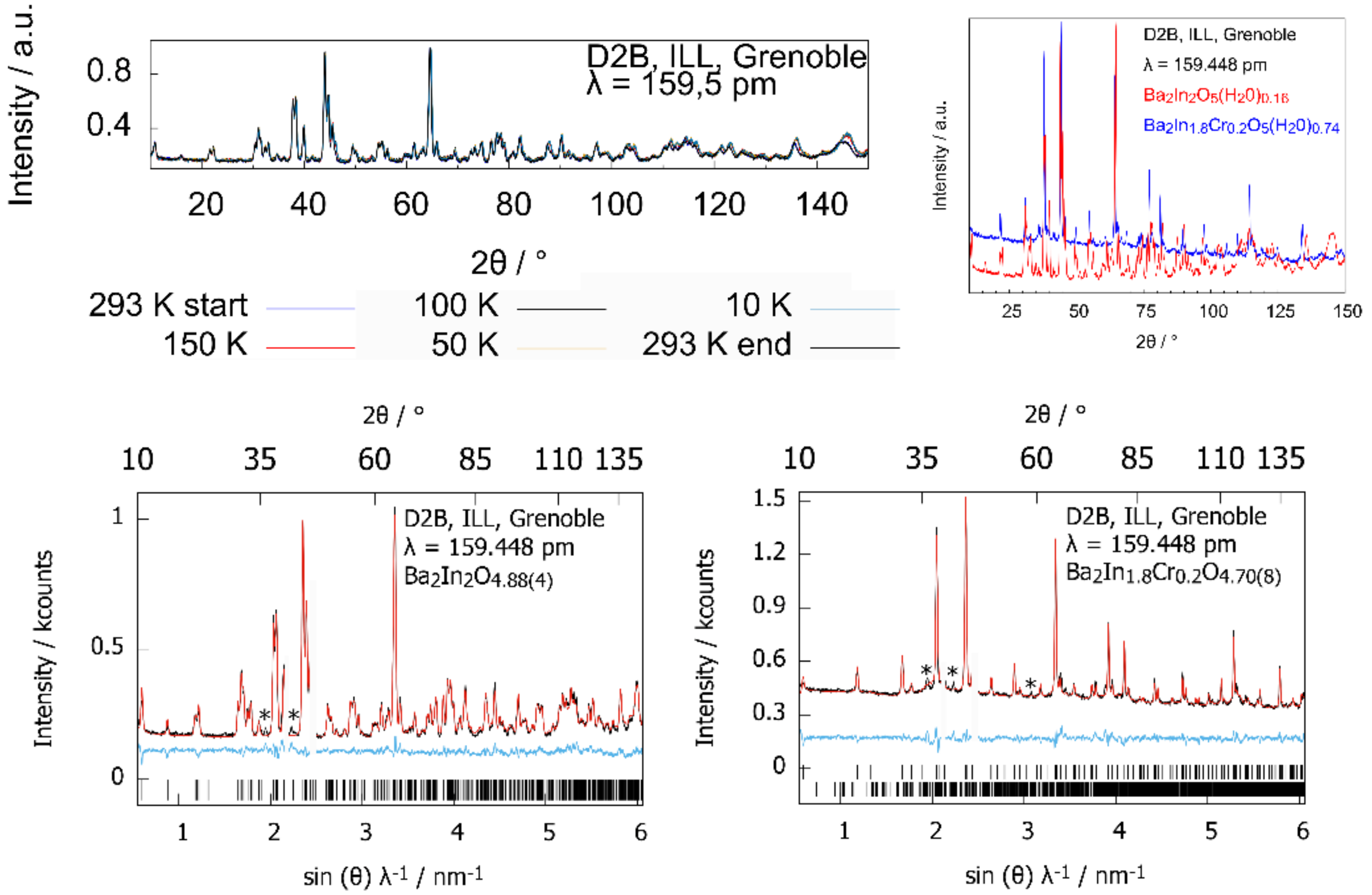

Fig. 1. Top left: Comparison of the normalized neutron diffraction data of $Ba_2In_2O_5(H_2O)_{0.16}$ between room temperature and 10 K, Numor 556649-556658, 556669-556678, 556679-556688, 556689-556698, 556699-556708, 556780-556789, top right: Comparison of the normalized collected high resolution neutron diffraction data of $Ba_2In_2O_5(H_2O)_{0.16}$ (Numor 556649-58) and $Ba_2In_{1.8}Cr_{0.2}O_5(H_2O)_{0.74}$ (Numor 556720-29) at 293 K bottom left: Rietveld refinements of the crystal structure of $Ba_2In_2O_{4.88(4)}$ (*Icmm*, a = 6.0781(3) Å, b = 16.7335(8) Å, c = 5.9493(3) Å) at 10 K, R_p: 3.31 %, R_{wp}: 4.30 %; Right: Rietveld refinements of the crystal structure of $Ba_2In_{1.8}Cr_{0.2}O_{4.70(8)}$ (Bragg marker on top, *I4cm*, a,b = 5.9821(2) Å, c = 16.946(1) Å, R_p: 2.14 %, R_{wp}: 2.88 %), side phase of $BaIn_2O_4$ (Bragg marker on bottom, 7.1(5) % phase fraction) at 10 K , excluded regions due to referred cryofurnace contribution, parasitic reflections marked with *, summarized data of Numor 556770-556779.

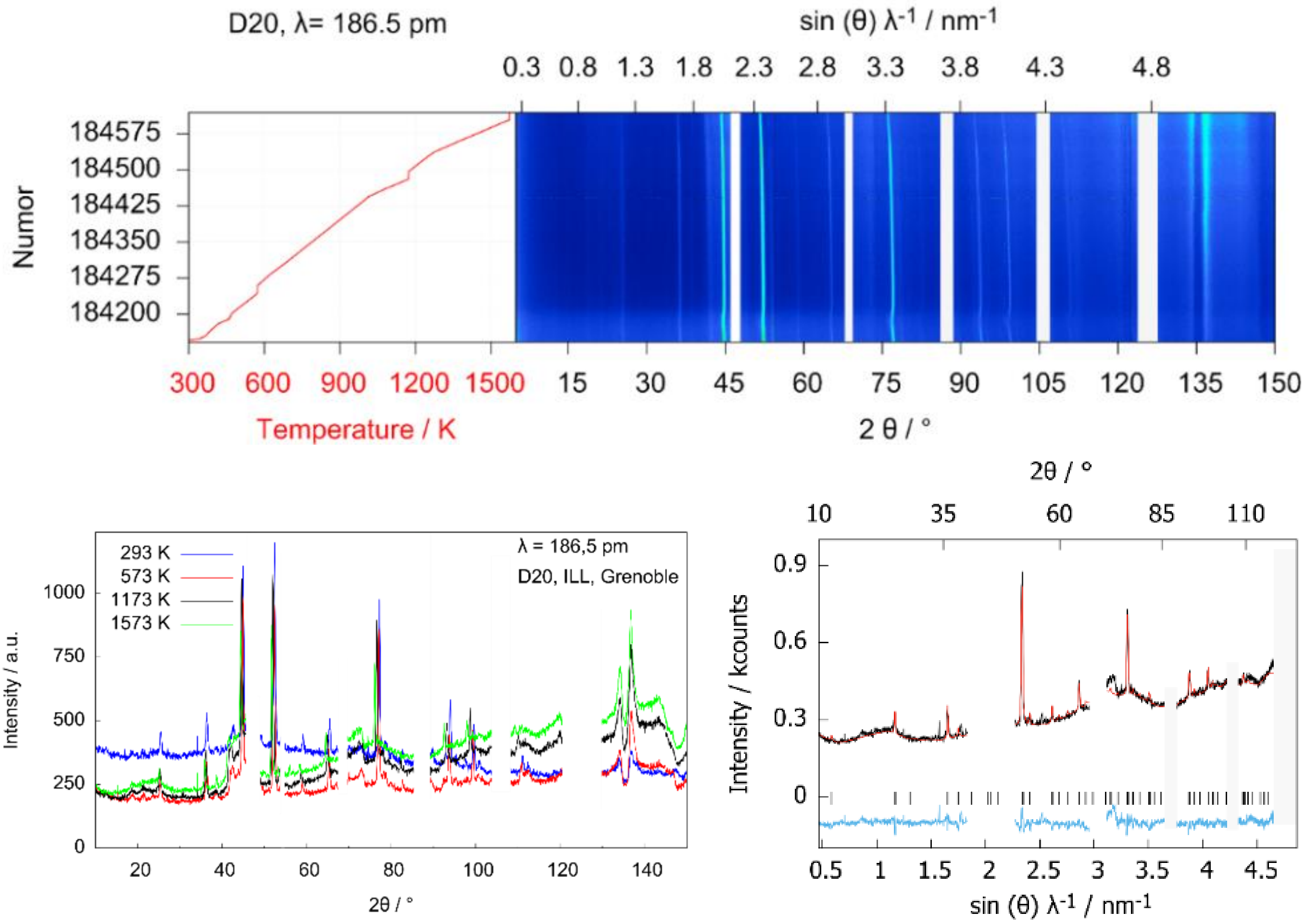

Fig. 2. Top : *In situ* neutron powder diffraction of the heating of $Ba_2In_{1.8}Cr_{0.2}O_5 \cdot 0.74H_2O$, temperature profile (top left), diffraction data plot in false colors, Nb foil contribution excluded (top middle), comparison of the collected diffraction data at chosen temperatures, Numor (184142, 184244-184260, 184481-184496, 184604-184619) (top right), Rietveld refinements of the crystal structure of $Ba_2In_{1.8}Cr_{0.2}O_{5.19(4)}$ (*I4cm*, *a*,*b* = 6.0598(9) Å, *c* = 17.094(4) Å, R_p: 3.23 %, R_{wp}: 2.95 %)) at 1573 K (bottom), excluded regions due to the Nb sample holder and contributions of the sapphire single-crystal sample holder.

References

[1] S.A. Speakman et al., *Solid State Ion*. **2002**, *149*, 247–259.
[2] M. Widenmeyer et al., *J. Membr. Sci.* **2020**, *595*, 117558.
[3] J.B. Goodenough et al., *Solid State Ion.* **1992**, *52*, 105–109.
[4] S. Yoon et al., *Solid State Sci*. **2017**, *73*, 1–6.
[5] H. Lei et al., *Ceram. Int.* **2018**, *44*, 19751-19755.